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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII NOVEMBER 1958 No. 11

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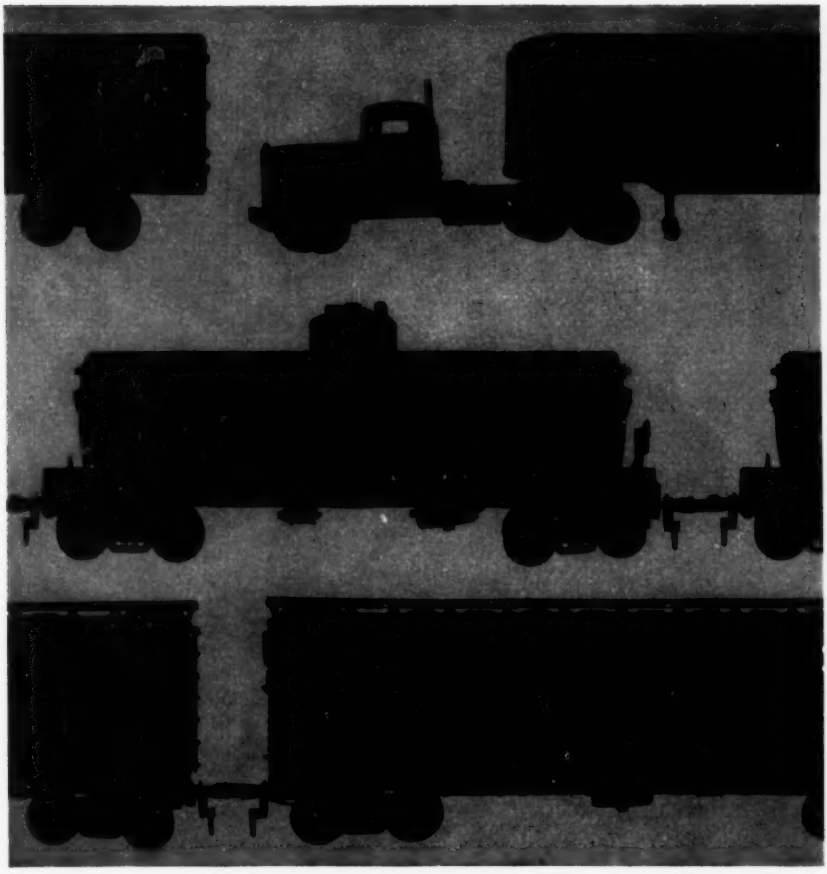

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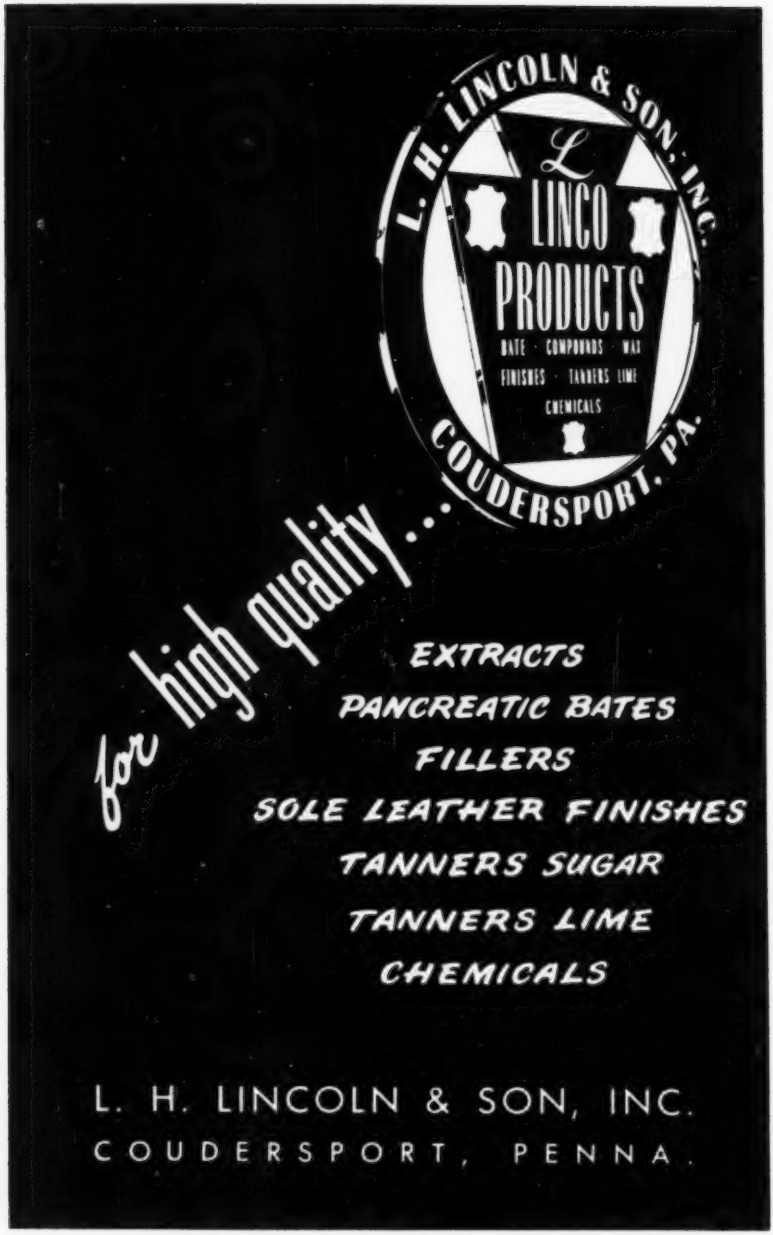
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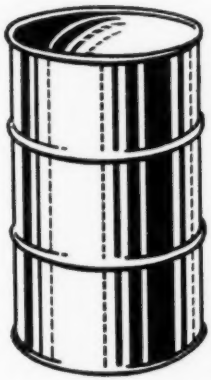

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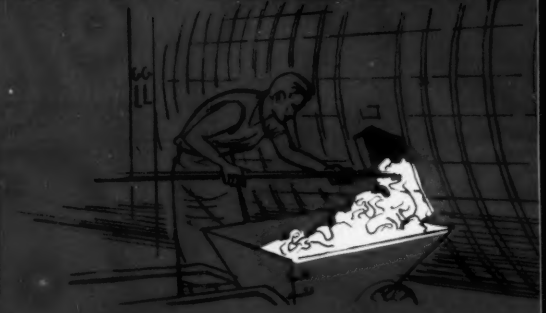

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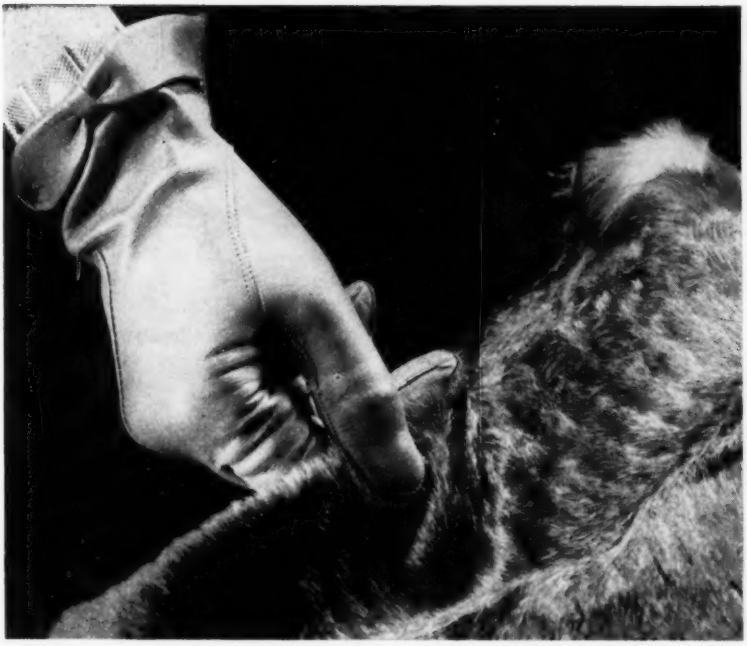

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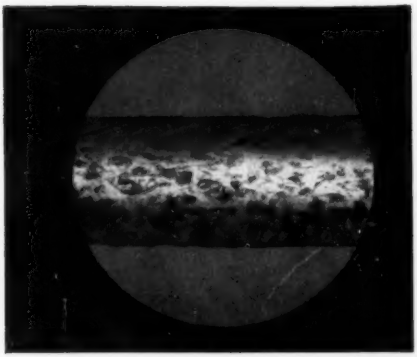

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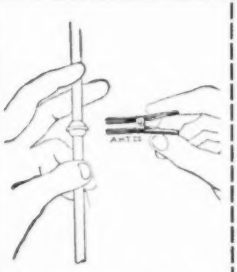

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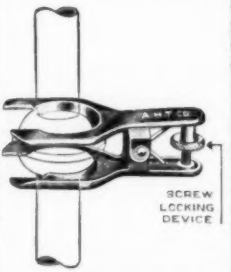

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.

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VARIOUS FACTORS RELATING TO QUALITY OF HIDE RAW STOCK FOR TANNERIES*

E. J. STRANDINE and F. G. CONNICK

Swift & Company
Chicago, Ill.

ABSTRACT

The effects of brining, as compared to ordinary green-salting, have been studied in large-scale curing tests. There is no significant difference in shrink or in leather yield, but brining brings about a more rapid cure, especially if the skins are fleshed first. Brined hides are cleaner than green-salted hides and are almost free from so-called salt stains, salt pits, and raw spots.

INTRODUCTION

Except for a relatively small percentage of fresh hides processed without curing, hides delivered to tanneries have been cured by either a brining process or by green-salting with rock salt. In both methods of curing a certain percentage of moisture and soluble protein is removed while salt is absorbed. Both kinds of cured hides produce good leather, but an increasing number of reports in the literature indicate that brined hides are superior in quality to green-salted hides, resulting in higher leather yields, reduced number of salt stains, and superior general quality of leather. In spite of these repeated reports in the literature, some questions still arise as to the advantage of brined hides as tannery raw stock.

The present paper reviews the two methods of curing hides and presents observations and results of laboratory tests as well as results from test packs sent to various tanneries.

Hausam (5, 6), DeBeukelaer (9), and Hauck and Lollar (4) have presented excellent reviews of the literature on curing of hides and skins. This literature has been concerned with the role of salt, preserving additives, bacterial growth on hides, and storage problems. Relatively few reports in the literature have compared the yields or quality of leather from brined and green-salted hides. In one of the early investigations McLaughlin and Theis (8) reported that hides cured by brining followed by salting produced a greater weight of leather and leather which was thicker and firmer than that from green-salted hides. DeBeukelaer (1) pointed out that brined hides (Heavy Colorado) produced higher white-weight gains and that the resulting leather was free of so-called salt stains.

*Presented at the Fifty-fourth Annual ALCA Meeting, Swampscott, Mass., May 26, 1958.

COMPARISON OF GREEN-SALTING AND BRINING

In conventional green-salting, the hides are spread flesh-side up in a pack, and a layer of salt is spread over the flesh surface. The salt slowly dissolves in the hide moisture, producing the curing brine which soaks into the hide while the excess brine with blood runs off. To prevent too great a run-off of brine and to insure uniform cure to all parts of the hide, the packs are built with a slope and the outer edges of hides are folded, producing a retaining wall which delays the run-off of brine. Successive layers of salt and hides are added to the pack until a height of 4 to 5 feet is obtained. Since the salt dissolves slowly and is absorbed only by diffusion, these hides usually remain in pack a considerable time to insure satisfactory and uniform curing. The usual practice is to keep the hides in pack 30 days.

In brine-curing, the hides are placed in a vat of saturated brine, which comes in contact immediately with all parts of the hide. The hides are agitated, bringing fresh saturated brine in contact with both the flesh and grain surfaces. The brine is kept saturated by circulating the brine through a salt-box or Lixator, or by having excess salt in the brining vat. Keeping the brine saturated and the hides agitated is of utmost importance if the hides are to be rapidly and uniformly saturated with salt. After 16–24 hours in the saturated brine the hides are removed, drained, and then placed in a pack. No further salting is necessary, and the excess brine slowly drains from the pack. After draining for a few days, the hides are ready for bundling for shipment. At some plants the brined hides are allowed to drain in a steep bank or over a rack from 12–24 hours, after which they are bundled for shipment.

During brining, considerable dirt, clay, manure, and urine are removed, resulting in cleaner hides. Since the hides are floating freely in the brine and are not held flat as when in a pack, the hides will contract in area and appear plumper than similar hides held flat in a pack. When put back into soak at the tannery, the brined hides will resume their original area. Thus, brined hides may appear plumper in the cured state.

Typical analyses from the bend area of unfleshed brined and green-salted hides produced by commercial methods of handling are shown in Table I. The brined hides were brined overnight, drained a few hours, and held in pack at least 30 days, while the green-salted hides were in pack at least 30 days.

Numerous analyses have shown that brined hides contain as much salt as green-salted hides and are as fully saturated with salt.

RELATIONSHIP BETWEEN THE LENGTH OF TIME BRINED HIDES ARE HELD IN PACK AND THE RESULTING SHRINK AND LEATHER YIELD

Four test lots of native steerhides were weighed after trimming, brined overnight in saturated brine, and put into conventional packs for draining.

TABLE I

COMPARATIVE ANALYSES OF BRINED AND GREEN-SALTED STEER HIDES AT TIME OF SHIPMENT

	Green-salted	Brined
Av. % H_2O	43.9	40.0
Av. % NaCl	13.74	14.16
Ratio H_2O/NaCl	3.19	2.82
NaCl in the solution in hides, %	23.8	26.13
Saturation, %	90.3	99.0
Time in pack	10 weeks	8 weeks

Each pack contained approximately 800 hides. After being held in storage for 2, 4, 6, and 8 weeks, the packs were shipped to a tannery for processing. All test packs were given identical processing at the tannery, being vegetable-tanned for belting leather. Data on shrinks after brining and storage as well as the leather yields are given in Table II.

The results in Table II demonstrate that very little difference in shrink was obtained in the packs held in storage for 2, 4, 6, or 8 weeks. This indicates that brined hides are well-cured and ready for shipment after being held in pack for two weeks after the overnight brining period. The tannery results indicated that no significant difference in leather yield on the four test lots was obtained. The tannery report also showed that all the lots were well-cured and in excellent condition.

TABLE II

COMPARISON OF SHRINK AND LEATHER YIELDS ON BRINED HIDES HELD FOR VARIOUS TIMES PRIOR TO SHIPMENT

	Held 2 Weeks	Held 4 Weeks	Held 6 Weeks	Held 8 Weeks
No. of hides	808	772	816	781
Total green wt. (lb.)	58,800	58,358	59,134	58,774
Total net shipping wt. (lb.)	46,516	46,090	46,523	46,395
Loss in weight (lb.)	12,284	12,268	12,611	12,379
Shrinkage, %	20.90	21.02	21.33	21.06
White-wt. yield, %	98.29	97.82	99.34	96.56
Total yield based on shipping wt., %	61.95	62.25	63.42	61.90
Total yield based on white wt., %	63.02	63.64	63.83	64.10
Total yield based on blood wt. less manures, %	49.01	49.18	49.92	48.88

COMPARISON OF LEATHER YIELDS FROM BRINED AND GREEN-SALTED HIDES

Four test packs, one of brined cowhides, one of brined steerhides, one of green-salted cowhides, and one of green-salted steerhides, were put down. In selecting the test lots, each purchase lot of steers or cows was divided equally so that alternate hides went into the brined test lot or the green-salted test lot. Test lots were held under similar conditions of pressure (height of pack), temperature (60° F.), and time (30 days). After storage the hides were taken up, bundled, and shipped to a tannery for processing.

TABLE III

COMPARATIVE CURING SHRINKS AND LEATHER YIELDS ON BRINED AND GREEN-SALTED STEERHIDES AND COWHIDES

	Green-salted Steerhides	Brined Steerhides	Green-salted Cowhides	Brined Cowhides
No. of hides	600	600	802	801
Total green wt. (lb.)	51,330	51,271	55,325	55,111
Gross shipping wt. (lb.)	41,344	41,037	45,718	44,198
Net shipping wt. (lb.)	39,844	41,037	44,036	44,198
Shrinkage (lb.)	11,486	10,234	11,289	10,913
Shrinkage, %	22.38	19.96	20.40	19.80
White weight, %	72.22	69.13	70.95	68.07
Actual yield, %	74.18	71.16	74.13	74.05
Actual yield (based on equal shrinkage of 18.0%), %	70.22	69.46	71.96	72.42

The data obtained from the tests (Table III) indicated that the hides from all the packs were well-cured, had satisfactory shrinks, and produced good yields of leather. When calculated on an equal shrink basis, the brined steerhides showed 0.76% less yield than the green-salted steerhides, while the brined cowhides showed 0.46% greater yield than the green-salted cowhides. The tannery report indicated that as far as the quality and selection of leather from the four lots were concerned, the brined lots were superior or equal to the green-salted hides.

EFFECT OF FLESHING OF HIDES PRIOR TO CURING

Pieces of fresh steerhide were hand-fleshed and brined in saturated brine and compared with adjacent pieces which were unfleshed. The hide pieces were brined at 65°–70° F. in saturated brine with excess salt present and with intermittent agitation, using a ratio of four parts by weight of brine to one part of hide. Results of various brining tests on fleshed and unfleshed hide pieces are shown in Table IV.

TABLE IV

EFFECT OF FLESHING ON BRINING SHRINKS OF FRESH STEERHIDES

(Average of 4 Tests)

Brining Time	Shrink—Based on Unwashed Wt.*		Shrink—Based on Washed Wt.	
	Unfleshed	Fleshed	Unfleshed	Fleshed
4 hr.	− 7.7	−10.8	− 5.2	− 9.1
8 hr.	−11.4	−14.5	− 8.7	−11.5
12 hr.	−11.5	−14.4	− 9.8	−12.8
16 hr.	−10.8	−16.9	− 9.3	−14.7
20 hr.	−13.2	−16.8	−11.7	−15.8
24 hr.	−12.4	−16.3	−10.7	−15.0

*Average percentage of fleshings compared to unfleshed weight:—16.5%.

Results in Table IV are based on weights of laboratory-test hide pieces after draining for one hour after brining. In actual commercial practice, hides are bank-drained 12–24 hours or are put into packs for from 2 to 8 weeks. This results in additional shrinks due to draining and to the pressure caused by the weight of a pack. After two weeks in a pack very little additional shrink occurs (Table II). These relationships in shrink are shown in Fig. 1.

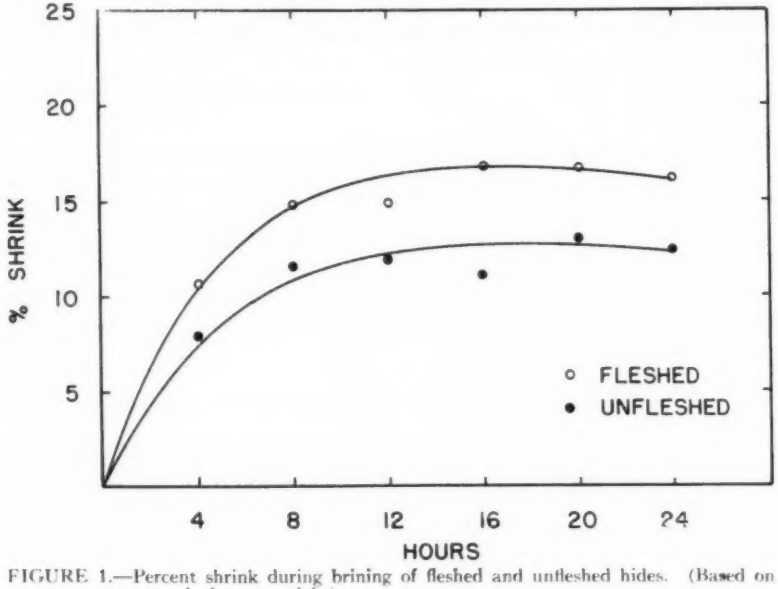

FIGURE 1.—Percent shrink during brining of fleshed and unfleshed hides. (Based on unwashed green weight)

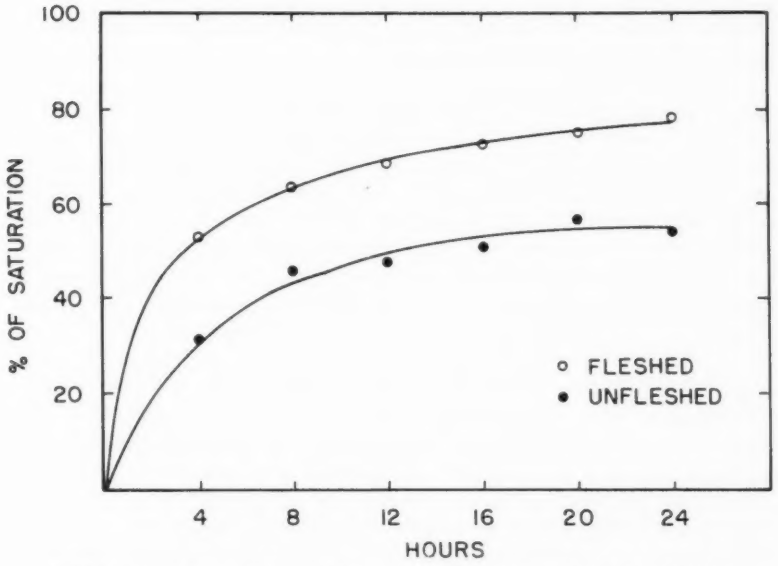

FIGURE 2.—Effect of fleshing prior to curing on salt saturation in brined hides.

Analyses of the brined hide pieces (laboratory tests) with and without fleshing prior to brining are shown in Table V and Fig. 2. A representative half of each of the samples of the unfleshed hide pieces was fleshed after brining, the remaining collagenous portion being analyzed for salt and moisture for comparison with the unfleshed portion.

TABLE V

ANALYSIS OF FLESHED AND UNFLESHED BRINED HIDES

(Average of 4 Tests)

Brining Time	Fleshed Hide			Unfleshed Hide			Collagen of Unfleshed Hide		
	% H_2O	% NaCl	% Sat.	% H_2O	% NaCl	% Sat.	% H_2O	% NaCl	% Sat.
4 hr.	52.5	8.45	52.5	52.9	4.74	31.1	54.2	4.71	30.3
8 hr.	49.3	9.82	62.9	48.0	6.51	45.2	49.7	6.23	42.2
12 hr.	48.4	10.37	66.7	49.4	7.00	47.0	49.2	7.54	50.3
16 hr.	46.0	10.86	72.4	45.3	6.90	50.1	45.0	6.91	50.4
20 hr.	42.5	10.42	74.6	42.3	7.38	56.1	45.3	8.12	57.6
24 hr.	43.3	11.15	77.7	43.7	7.56	54.9	45.4	7.18	51.8

After 24 hours of brining and 1 hour of draining, the liquid in fleshed hide pieces had an average salt saturation of 77.7% while the unfleshed pieces averaged only 54.9% saturation. The liquid in the dermal or collagenous portion of the skin was 51.8% saturated with salt, or only slightly less than the whole unfleshed hide. These results demonstrate that adipose tissue on the hides delays the absorption of salt, whereas fleshing prior to curing increases the rate of salt absorption. It should be pointed out that these laboratory tests differ from commercial brining practices in that the laboratory samples were analyzed after one hour of draining whereas commercially brined hides are drained 24 hours or longer. In commercial brining of hides, the hides are agitated continuously during the early part of the brining period and intermittently a portion of each succeeding hour.

MISCELLANEOUS OBSERVATIONS ON CURED HIDES

Contamination after curing.—From time to time tanners encounter stains or discoloration in a small percentage of the hides after unhairing or tanning. Spectrographic analyses of these discolored areas have shown the presence of iron, lead, and other heavy metal salts, which have sometimes been traced back to contamination of the hides in the cars during shipment. A thin inconspicuous layer of contaminating dust on the floor or sides of a car may be sufficient to result in serious discoloration of the hides when sulfided or tanned. Shipment of hides in cars which have previously been used to ship creosote-impregnated posts or ties has also been known to result in permanent stains in the leather.

So-called salt-stains.—Considerable reference is made in the literature to discolorations in leather supposedly caused by certain strains of bacteria or to traces of impurities in the salt, e.g., calcium, magnesium, or iron. Test hides were cured with NaCl to which the above chemicals were added. Hides were held at 100°F. in sealed jars for 4 months, opened regularly for inspection, and at the end of the test, soaked, limed and sulfided, and unhaired. Only the hides cured with salt plus added iron salts showed any discoloration or spots.

A report from a heavy sole leather tanner on 100 shipments of brined hides and green-salted hides shows that of 83 salted shipments only 3 were free of "salt stains" in some degree while no "salt stains" were found in any of the 17 brined shipments.

To quote this tanner, "Brine-cured hides rarely show any 'salt-stains' whereas salt-cured hides are rarely completely without some 'salt-stains'. This, to me, is sufficient evidence to state flatly that the chance of 'salt-stains' is almost eliminated by brine-curing."

Another tanner says, "Speaking from the standpoint of side leather opertions, we see no salt pits or salt stains on brine-cured hides."

"Salt-pits" or low spots.—Heavy-leather tanners are often plagued with a condition in the finished leather in which a small percentage of the leather appears to be pitted or to have small depressions or low spots. These have been attributed to large rock salt crystals or pieces of shale in the rock salt which became pressed into the hide by the weight of the hides above it in the pack. Impressions from the salt and shale can be observed in green-salted hides coming out of pack, but after soaking, liming, and unhairing, these marks disappear. A tanner who uses both green-salted and brined hides had this to say about the percentage of "salt-pits" in brined hides: "The percent (in brined hides) is very small, but it is there occasionally, which proves to me the term salt-pit is incorrect. Here again I would say that brine-curing helps to minimize low-spot damage." Apparently some factor other than salt or shale is responsible for the low-spot damage. More work is needed to clarify this problem.

Raw untanned layers.—Another defect in heavy leather is the presence of raw untanned layers in the center of the hide, which become apparent when the hide is cut into soles or buffed for belting. Examination of the cut surface shows that the tan liquors failed to strike through completely, leaving dried raw areas not reached by the tannin that penetrated from both the grain and flesh sides. Some tanners have attempted to correlate this condition with similar layers in unhaired hides where the lime failed to penetrate completely and resulted in difficult unhairing of patches of hair. A report from a tanner states, "We are less prone to have the condition show up in brined hides, and the possibility is further reduced by green-fleshing".

DISCUSSION

When is a hide fully cured?—A hide can be said to be satisfactorily cured when the collagenous portions of the hide can be held without deterioration and subsequently processed into satisfactory leather. A fully cured hide will have sufficient salt and a sufficiently reduced moisture content so that bacterial growth and autolytic enzyme activity are retarded or inhibited. Numerous analyses as well as the data submitted in this report demonstrate that hides properly brine-cured contain as high a level of salt concentration as green-salted hides. Tancous (12) reported that brined hides had higher moisture content and lower salt content than green-salted hides. This may happen if excess salt is not present with the brine to keep the brine saturated at all times. Agitation is also required if near-saturation of brine in the hides is to be attained.

Cured hides (85–100% saturated with salt) can be stored for long periods of time, depending upon the degree of salt saturation in the hides and depending upon the temperature and humidity of storage (Koppenhoeffer and Somer, 7). Higher temperatures and humidities are favorable for bac-

terial growth, especially for the salt-tolerant bacteria. It is not the percentage of salt or moisture that is important in determining bacterial growth but the degree of saturation of the brine in the cured hides. Stuart and Frey (10) reported that bacterial growth on hides increased rapidly when the moisture content of the hides increased above 49.2% (83.3% saturated). However, as the moisture content increased, the percentage of salt decreased, resulting in brines in the hide which were only 77.3% and 75.4% saturated. Keeping the moisture in the hide saturated with salt will retard bacterial growth.

Curing and enzyme activity.—Saturating the hide moisture with salt appears to have an inhibiting effect upon the natural autolytic enzymes present in the hide. These enzymes may be proteolytic such as the cathepsin complex (Fruton *et. al.*, 2, 3) or lypolytic. Since enzymes are protein in nature, it may be that the enzymes are "salted-out" or inactivated when the salt concentration reaches a certain level in the hide. Bacterial growth may result in the production of various enzymes, some of which may attack the collagen (collagenases) whereas others may attack globular proteins or fats.

Enzymatic attack resulting in "hair slip" will not always be indicative of deleterious action on collagen, since "hair-slipped" hides often produce leather with satisfactory grain, break, and strength. At other times apparently collagenase activity has been present, since the skin is very weak and can be torn easily, although no apparent hair slip is observed. It should be pointed out that various enzymes may be present in cured hides, but that hides fully saturated with brine are less susceptible to enzyme and bacterial attack, especially if the hides are stored at low temperatures and humidities.

Small quantities of preservatives added to the brine kill or inhibit the growth of bacteria and molds, whereas certain salts inactivate the natural autolytic enzymes in the skin, thus increasing the storage life of the hides. Various oxidizing agents such as sodium hypochlorite, hydrogen peroxide, and perborates have been used in the past. Many salts such as borax, sodium silicofluoride, sodium fluoride, sodium carbonate, zinc oxide, and zinc sulfate have been recommended. Numerous halogenated phenolic derivatives have been reported as having beneficial effects in hide-brining. It appears that very few if any of the known chemicals when used in economical quantities in hide brine will inhibit or destroy all strains of bacteria and molds. Some chemicals appear to inhibit molds better than bacteria or vice versa.

Fleshing.—The amount of subcutaneous fatty tissue adhering to a hide varies with the "take-off" and with the condition or "finish" of the cattle from which the hide was removed. Theoretically, fatty tissue should retard salt absorption but not completely stop it, since fatty tissue is not solid fat but contains significant amounts of moisture (15% to 40%) in the fat cell walls and in the connective tissues between the fat cells. Salt dissolves in

the moisture of the adipose tissue and slowly but eventually diffuses into the dermis and epidermis of the hide. Stuart and Frey (11) reported that fat tissue on hides retarded the absorption of salt during green-salting, while our tests reported here indicate that the same is true for brine-curing but to a much smaller degree. Their results on green-salting indicated that the unfleshed green-salted hides were 40.0% saturated with salt after 24 hours of green-salting compared with the fleshed green-salted hides which were 81.4% saturated. Our results show that the unfleshed brined hides and fleshed brined hides were 54.9% and 77.7% saturated respectively after 24 hours of brining. The difference in the effect of adipose tissue in retarding salt absorption during brining and green-salting is explainable on the basis that in brining, the hides are immediately exposed to saturated brine, whereas in green-salting, the salt must dissolve without the aid of any agitation before it can start to penetrate the adipose tissue. This again illustrates the advantage of brine-curing over green-salting of hides, which always contain a certain amount of adipose tissue.

Brining, green-salting, and leather yields.—Since leather yield is based on the invoiced weight, it will be directly related to the shrink (moisture and dirt loss) of the hides during curing. The greater the quantity of extraneous material (dirt, manure, moisture etc.) removed from the hides, the greater will be the shrink and the yield of leather. When hides are given equal shrink, the yield of leather from brined hides will equal that of green-salted hides.

CONCLUSIONS

1. Brined hides held in pack show very little increase in shrink after two weeks storage, and this small increase in shrink is reflected in a small increase in leather yield.
2. Comparison of results of brined and green-salted steerhides and cowhides shows no significant difference in shrink or in the yield of leather.
3. Brining removes much of the dirt adhering to the hair side of a hide resulting in cleaner hides and less extraneous material to ship.
4. Fleshing hides prior to brine-curing increases the rate of salt absorption.
5. Preservatives added to brine increase the storage life of hides by inhibiting bacterial growth and autolytic enzyme activity.
6. Certain stains in hides are attributable to contamination during shipment.
7. So-called salt-stains, salt-pits, and raw spots are absent or nearly absent from brine-cured hides.

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DISCUSSION

Dr. T. C. Thorstensen (Lowell Technological Institute Research Foundation): Dr. Strandine defined cure in his paper by saying, "A hide can be said to be satisfactorily cured when the collagenous portions of the hide can be held without deterioration and subsequently processed into satisfactory leather." During the past few years, particularly the last ten or so, labor costs have gone up considerably. Our hides have become larger and thicker and much more full of fat. Also, there has been a great desire for economic reasons to get a fast turnover and reduction of inventories. These factors must inevitably result in poorer cure. This has been evidenced by hair slip, veininess, loose break, weak leather, and in some cases, rotten spots.

During the recent meeting of the National Hide Association in Florida, some very strong statements were made by tanners concerning the advantages of brine-cured hides. Since brine-curing benefits both the packer and the tanner alike, we can expect to see much more of it in the future.

Dr. Strandine has shown us some very interesting data. I was particularly interested in the laboratory investigation of the effects of fleshing. These data show that you get a faster cure and better penetration of the salt with the fleshed hide. The question comes to mind as to whether demanuring, trimming, and fleshing, followed by a conventional cure, would not possibly be of value. I wonder if that has been considered at all by any of the packers, since it would result in a labor saving for the tanner, give better cure, and reduce shipping costs.

I would like to question the tanners present, and also Dr. Strandine, about the soaking of brined hides. Do you find that brined hides behave differently in your soak and in your processing? Or do you process them the same as green-salted hides? If there are differences, what are they?

DR. STRANDINE: To answer Dr. Thorstensen's first question, I agree with him that it certainly would be advantageous to have fleshed hides which are green-salted or brined—primarily brined. Our company at one plant has done some work on the fleshing of hides followed by a brine cure. These hides were cured very well and resulted in satisfactory leather. We are at the present time contemplating going to a second plant where we will flesh hides and follow with brine-curing. But I cannot speak from any experience about the process of fleshing followed by conventional green-salting. Maybe somebody else here can answer that question.

DR. THORSTENSEN: Very possibly the process has not been considered at all. It is just an idea that occurred to me. The second question I asked the tanners present, and also you, Dr. Strandine, concerns the processing of brined hides as compared with green-salted hides in the tannery. Is there a difference in the plumping that takes place in the soaking, and are different soak methods needed or recommended?

DR. STRANDINE: I have not had too much tannery experience, but I have heard from one source that where they do handle brined hides, the brined hides seem to soak back faster than the green-salted hides, and they also can shorten their liming times somewhat. As I say, this is not from personal experience. It is just from hearsay. And I personally would be interested to hear what some tanners can say on that subject, because from time to time people ask us if they should handle brined hides differently at the tannery than they handle green-salted hides.

G. WALTER SCHULTZ (Elkland Leather Co., Elkland, Pennsylvania): May I make a statement at this time rather than answer the question? I do not think anyone will deny that brining offers better possibilities than the conventional green-salting, as witness the frigorifico hides we had before World War II, which left little to be desired as raw material. But my experience with domestic brined hides over the last two years has been highly unsatisfactory. I would say they were little if any better—some probably not as good—as so-called small-packer cure.

I have tried to find an explanation for this, because I did participate in some of the tests that Dr. DeBeukelaer made some years ago, when brined hides were produced that were an improvement over regular green-salted hides. Anyone who has had experience in converting pilot-plant tests into

factory operation knows that he does not always get what he wants, which may explain the undesirable characteristics that we have in commercial brine-cured hides today. They are not cured to the extent that they should be. We have found that just in transporting them to the tannery, which may mean a week in a boxcar, they will show evidence of decomposition on arrival. They will be slippery, with the hair loosened, and in some cases will show actual grain damage.

Normally, we want a cured hide that will keep at least three months without any deterioration. If the so-called brine-cured hides are processed immediately on arrival at the tannery, they may not show any salt stain or other damage unless they have deteriorated in transit. The same result can be had with fresh hides—if they are processed quickly enough to avoid deterioration. My personal impression is that these brined hides are not dehydrated sufficiently to effect a satisfactory cure.

DR. STRANDINE: I would like to ask Mr. Schultz if any analysis for salt and moisture was made of these hides that you said did not hold up during shipment. If they did not keep during shipment, it would indicate to me that they had not been properly cured—that there had been some slip-up somewhere. We have found that when hides are properly cured, you can store them for years. We have many customers who have used brined hides repeatedly over the last 20 years and have found them satisfactory. I think Dr. DeBeukelaer reported on tests in which brined hides were stored for five years with very little change. Of course these were stored under refrigerated conditions and not shipping-car conditions.

MR. SCHULTZ: All brined hides that we have worked, off and on over the past several years, have shown that they have to be soaked promptly to avoid undesirable results.

C. DAVID WILSON (Fred Rueping Leather Company): Using percent saturation as a criterion, can I conclude from Table VI that 24 hours of brining is not enough?

DR. STRANDINE: No, in commercial brine-curing where the hides are agitated and the brine is kept saturated, 24 hours of brining will result in high enough salt saturation to result in a good cure. It should be pointed out that the particular test reported here was done in the laboratory. The analysis was made after the hides had been brined for 24 hours with intermittent agitation and given a one-hour drain. However, in commercial practice, as shown in the first slide, you will notice that we had from 90 to 99% saturation. Longer agitation, such as obtained in commercial brining, will result in a higher percentage of saturation than intermittent agita-

tion in the laboratory. Analyses of a hide after one hour of draining and after 24 hours of draining will also show some differences. These laboratory tests were made to study the relative effects of the fleshing; in other words, to see what effect the fat had on the rate of salt absorption.

DR. LOLLAR (Tanners' Council Laboratory, University of Cincinnati): Dr. Thorstensen, I would like to comment on a bit of auxiliary information in this regard. From analyses made on hides commercially cured in the newer vat-brining process, on defleshed hides, it has been my observation that 24 hours is not sufficient and that 48 hours is necessary under those conditions; there is an increase in the amount of salt in the hide from 24 to 36 to 48 hours of holding in the vat. I do not want to compare that to the older brine-curing process. I am talking specifically about the vat-brining which has come into use more recently.

DR. THORSTENSEN: It seems to me we are talking here of a laboratory test. We should not overlook that fact.

DR. STRANDINE: Also, in commenting about the newer 48-hour vat-processing that Dr. Lollar spoke about, it should be pointed out that in that process there is no agitation of the hides whatsoever. The hides are merely placed in the saturated brine with layers of salt. And a longer brining period is required than in a process where the hides are agitated.

DR. LOLLAR: I should also have said that I found 48 hours does give complete saturation.

HAROLD BERNARD (G. Levor & Company): When you compared the green-salt and brine methods of salting, you failed to state whether you used rock salt or evaporated salt in your comparisons. You get a lot of stains of iron and such from rock salt but not from evaporated salt. Have you made any comparisons between the two methods of green-salting?

DR. STRANDINE: No. In the tests on green-salting we used a heavy rock salt. We did not use any evaporated salt.

MR. WHITMORE: We ran some of those hides—the ones that Dr. Strandine mentioned that were stored as long as five years. They did not work satisfactorily in the plant. They did not swell up in the limes, and we could not get a satisfactory fleshing job. I don't know what happened. But something happened to the fibers, particularly the flesh fibers, during the storage time.

MR. SCHULTZ: In the first tabulation that Dr. Strandine put on the screen, there was a yield of 61 to 63%. That is not a good yield on any type of hide. Even mid-winter hides ought to make a better yield than that.

DR. THORSTENSEN: That yield was equivalent for both cures. Whether the figure is high or low it should be about the same.

DR. TURLEY: You asked about any necessary differences in the processing of brined hides. What Mr. Whitmore mentioned just now reminded me of an interesting phenomenon I came across a year ago. In one tannery it was the custom to wash green-salted hides about twenty minutes in a drum, flesh, and then put into the lime. Well, some brined hides were put through the same process, and the effect was amazing. I suppose because they were more dehydrated, the twenty minutes was not sufficient time for the fibers to come back and make a uniform soaking job. When the skins went through the fleshing machine, there was a corrugated effect—where the fibers had either swollen or not swollen back again. In this case it was necessary to increase the first soaking time very considerably.

THOMAS BLAIR (Saxe Cutch Corporation): I would like to answer a question that Dr. Thorstensen asked before, about whether it is necessary to change the soaking. In a couple of experiences with brined hides we found it was not necessary to soak at all—just wash the salt out, drain the paddle, fill it up, and go right ahead with the sulfiding. But to corroborate what Dr. Schultz said, we did find quite a bit of deterioration on one or two packs.

Quick Tanning Process. The hides are subjected to the ordinary treatment in running water, and then placed in a fulling trough hermetically closed. The water in the trough contains to every 100 pounds of hides weighed as taken from the water, a solution of 30 pounds of divi-divi, 20 pounds of bark of oak root, 30 pounds of alum, 65 pounds of acidulated barley meal, and 1 pound of sulphate of copper. The hides in the fulling trough are frequently turned for 24 hours, and then brought together with the tanning fluid into an ordinary vat, where for 15 to 20 days they are taken out daily and then put back again. After the expiration of this time they are put in tan in an ordinary pit, where they remain 15 to 30 days, when they are finished. In place of divi-divi and bark of oak root other materials containing tannin may be used, and sulphate of alumina may be substituted for alum, and sulphate of zinc, sulphate of ammonia, or other sulphates for sulphate of copper, the characteristic feature of this process being the use of the tannin and alum at the same time and in presence of the sulphate of copper.
—*The Techno-Chemical Receipt Book.* Philadelphia: Henry Carey Baird & Co., 1903.

A RAPID SOLE LEATHER TANNAGE WITH ALDEHYDES*

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ABSTRACT

A new method of tanning with aldehydes (1) pointed a way toward the making of sole leather by a rapid process in which conventional vegetable extracts could be partially or fully replaced by domestic materials.

After adjusting the stock to the proper pH in the manner described previously, it is possible to reach a shrinkage temperature of 90°C. or higher in less than 24 hours by tanning with a mixture of glyoxal and formaldehyde. Afterwards, it takes only a few hours to ready the hides for immersion in rockers. Here the pretannage with aldehyde allows the use of tail liquors that are over 40° Barkometer strong and also heated to 120°F. In pilot-plant experiments, it took only 3 to 5 days to obtain full penetration. The largest of these experiments in which lignosulfonate alone was employed is discussed in detail. Chemical and physical data concerning the finished leather are also presented, together with some observations concerning storageability of leather produced in earlier tests.

The new rapid tannage produces a flexible but sufficiently firm type of sole leather such as is in demand today, without a sacrifice of color or heat resistance.

INTRODUCTION

In a previous paper describing new methods of tanning with aldehydes (1) the idea was advanced of employing these in combination tannages using either vegetable extracts or their substitutes and replacement materials. Experiments of this kind have been conducted mainly on heavy leather which is consumed by the Armed Services in large quantities as soling material. Since conventional leather of this type is for the most part tanned

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with imported tanning materials, the U. S. Quartermaster Research & Engineering Center has a strong interest in developing alternate tannages which would reduce the reliance of our leather industry on imported tanning materials. However, unless a new domestic tanning process offers immediate advantages, for instance by accelerating the tannage or by imparting new properties to the leather, prospects of arousing interest in it in peacetime are dubious. Fortunately, these prerequisites seem to be fulfilled in the present case.

A number of tannery trials exploring the possibilities of starting the making of sole leather with an aldehyde tannage have been reported in *Footwear and Leather Series Report No. 11*, published recently (2). The experience gained by this test series and by subsequent laboratory experiments served as the basis for a new set of pilot tests. This paper will describe only the final experiment, the largest of the four, made on 20 hides. It will stress the incidental benefits of the new tanning process to the tanner and also give a full account of the physical and chemical properties of the resulting leather. Preliminary data in regard to aging properties will be presented for sole leather produced in earlier tannery trials described in the report already mentioned (2).

EXPERIMENTAL

An outline of the pilot-plant test is given in Table I. The tannage can be defined in short as a mixed aldehyde tannage followed by filling and loading with lignosulfonate only. The aldehydes employed were technical solutions of glyoxal and formaldehyde, in the ratio 6 to 1 which corresponds approximately to 5 to 1 for the pure aldehydes. The stock consisted of ten

TABLE I

OUTLINE OF RAPID SOLE LEATHER TANNAGE

(All quantities, unless otherwise stated, are based on 1000 *lb. white-weight.)*

Alkalizing (in paddle)		
Ratio, skin to liquor		1:5
Temperature		70°F.
$NaHCO_3$ (per 100 gal.)		42 lb.
Moles per liter		0.6
Na_2CO_3 (per 100 gal.)		52 lb.
Moles per liter		0.6
Running schedule:	run	2 hr.
	stop	4 hr.
	run	2 hr.

TABLE I *(Continued)*

Tannage (in drum)		
Volume of alkalizing liquor transferred		80 gal.
Temperature		70°F.
pH Value		9.5
Normality (total alkali)		1.2
Glyoxal (30%), in 10 gal. water at 75°F. (in 4 feeds)		70 lb.
Formaldehyde (36%), minimum (added with last glyoxal feed)		10 lb.
Running schedule	run (1st feed)	0.5 hr.
	rest	0.5 hr.
	run (2nd feed)	0.5 hr.
	rest	0.5 hr.
	run (3rd feed)	1.0 hr.
	rest	0.5 hr.
	run (4th feed)	1.5 hr.
	rest	overnight
	run	0.75 hr.
Drum speeds	1st day	7–8 rpm
	2nd day	17–19 rpm
Final shrink temperature		190°F.
Lowering pH Value (in drum)		
Discard one third of liquor		
Sulfuric acid		90 lb.
Total running time		2.5 hr.
Final pH value (liquor)		3.8
Retannage (in rockers)		
Tanning material		Sodium salt of hardwood lignosulfonate
1st Rocker		
Barkometer		45°
Temperature		120°F.
pH value		2.6
Days in rocker		1
2nd Rocker		
Barkometer		60°
Temperature		120°F.
pH value		2.2
Days in rocker		1
3rd Rocker		
Temperature (at start, falling to room temperature)		120°F.
Barkometer		Liquor from 2nd rocker, not strengthened
Days in rocker		3

sides taken after dehairing and fleshing, ten sides after bating, and the matching sides after further deliming in dilute acid.

In the new tanning process the hides, according to Table I, pass through four stages. The first stage has the function of equilibrating the hide with a non-swelling alkalizing liquor as postulated in the original paper (1). In a sole leather tannery, because of the scarcity of drums, paddles were used for this treatment. The liquors were made up from sodium bicarbonate and soda ash in the ratio that they are present in sodium sesquicarbonate, i.e., 1 mole $NaHCO_3$ to 1 mole Na_2CO_3. This latter compound may, of course, also be used. Other ratios of the two alkalies have been tried only experimentally. As Table I shows, the quantities employed corresponded to an initial normality of 1.8 with respect to total alkali and gave a pH of 9.5 and a normality of 1.6 as determined by titration after equilibrium with the hides was reached. However, in the interest of economy a normality of 1.2 has been successfully used.

In laboratory experiments the alkaline bath was reused 6 to 8 times without materially reducing the pH or impeding the tanning action. Its strength was brought up by simply adding dry sodium bicarbonate and soda ash, in the ratio 4 to 5, which is the same as in sodium sesquicarbonate.

The buffering capacity of bicarbonate prevents the glyoxal from undergoing decomposition by the Cannizzaro reaction, which becomes prevalent at pH values above 9.5. For the same reason good lime removal by washing the dehaired or even the bated stock is beneficial. Since in the pilot-plant test under discussion some hides were more thoroughly delimed than others, the lime content of the glyoxal tanning bath was probably lower than it would have been in the presence of only unbated stock. Maintaining a temperature of less than 85°F. in the tan drums is essential for the success of the tannage. In the light of evidence in the literature (3) it is not surprising that heating-up of the drums to 95°F. or more should be avoided. Practical steps to assure this included keeping shelves and pegs in the drums at a minimum and moving the stock intermittently at low speed, as Table I shows.

The length of pretreatment required in a tannery (in paddles) for full penetration of the hides with alkali has not been investigated systematically. Instead, the alkalizing operation always was started on Friday, with occasional agitation over the week end. In laboratory tests, however, some intermittent paddling at night was sufficient to reach equilibrium within 24 hours. On the other hand, this goal could be obtained in drums, in laboratory as well as in tannery tests, by moving the stock at about 18 rpm for only 2½ hours on the first day and another hour the next morning.

In earlier experiments with glyoxal the hides assumed a yellowish color in the outer layers but stayed cream-white in the center even though the shrinkage temperatures rose to 190°F. It was found, however, that by the addition of 1% formaldehyde a uniform light color can be obtained throughout the heaviest part of the hide.

Other acids besides sulfuric acid, notably formic and hydrochloric acid, have been used successfully during the third stage of the process for lowering the pH after the tannage. In earlier trials the spent liquor from the tannage was discarded before lowering the pH of the stock, and a freshly prepared sodium chloride or other salt solution was added prior to neutralizing the hides. It was found, however, that this step was unnecessary. The evolution of carbon dioxide during acidification can be better controlled in drums which are open on both sides. Caution is required to avoid losses in the tub or damage to the drum.

It is desirable to bring the pH down to the vicinity of the range prevalent in the rocker retannage, which is about 2.6. If the pH of the hides is lowered to 3.5 to 4.0, the pH of the rockers will not rise unduly. Exclusive of necessary steps to make the measurements, this pH can be reached within 2 hours. Another half hour of drumming has essentially the purpose of making sure equilibrium has actually been attained. Once the proper amount of acid for a given load has been found, the sampling for pH measurements at frequent intervals can be dispensed with. In the final stages a single feed of acid must be no larger than ¼% on the white weight. It is also necessary to cut a sample taken from the butt area of a hide into little cubes and to shake them in a small volume of water for several minutes in order to determine the pH of the stock more correctly than by taking the pH of the liquor in the drum.

Rinsing of the stock before placing it in the rocker vats is favored in order to avoid the accumulation of salts in the retan liquors but has not been practiced in most tannery trials. Wringing-out under high pressure has been found very effective in removing excess salts and also in promoting penetration of the tan liquor in the vats.

Laboratory trials showed that under a given set of conditions, as in a rocker system, the type of lignosulfonate employed determines the degree of tannage obtainable. On the basis of a number of small-scale tests the sodium salt of hardwood lignosulfonate was selected for the 4 pilot-plant tests of which this paper describes the last one, in preference to the sodium salt of softwood lignosulfonate and to the magnesium salt. All 3 types, incidentally, form viscous pastes when mixed with water in equal proportions, in contrast to the unfractionated spruce extracts which give very fluid solutions. The low affinity of these raw, unfractionated liquors for hide substance is well known.

Since the final experiment was twice as large as the preceding three, it required two rocker vats. The lignosulfonate liquor left over from the earlier tests was strengthened by fresh material until a barkometer reading of 45° was reached. It was heated to 120°F. and at the same time adjusted to pH 2.6 by additions of sulfuric acid, and then fed to the vats which had a capacity of 400 gal. each. The next day the liquor was returned to the

storage tubs and strengthened with 300 lb. fresh lignosulfonate to read 60° Bk. The pH which was now 3.2 was lowered to 2.2 by the addition of about 20 lb. concentrated sulfuric acid per 1000 lb. white-weight. The liberal use of sulfuric acid for lowering the pH in the rocker vats has the purpose of increasing the degree of tannage. Maximum fixation of lignosulfonate, according to many investigations, can only be attained in the vicinity of pH 2 (4) or at most pH 2.5 (5). In order to avoid acid deterioration of the resulting leather, the pH must be raised again in the oil wheel. As Table II shows, the 3 sides retanned with a blend of spruce and vegetable extracts acquired a higher pH than the lignosulfonate-retanned sides when oil-wheeled together, because of the initial pH difference.

TABLE II

ANALYSES AND TESTS ON RAPID-TANNED SOLE LEATHERS

	Beamhouse Treatment			
	a 3 backs, dehaired and fleshed	b Matching backs to (a), bated and delimed	c 1 back each, dehaired, bated, delimed	d Matching backs to (c), with same beamhouse treatments
Domestic extract (lignosulfonate) in rockers, %	100	100	100	30
*Analyses of composite samples**				
Water solubles, %	24.7	23.9	21.4	24.3
Hide substance, %	47.8	48.9	50.1	44.4
Grease, %	2.9	3.4	3.2	2.6
Insoluble ash, %	0.3	0.3	0.3	0.2
Degree of tannage	50.8	48.0	50.0	64.2
pH value	3.3	3.3	3.4	3.7
Physical tests				
Compressibility, %	9.7	9.9	10.9	9.5
Density	0.93	0.93	0.94	0.97
†Shrink temperature				
in water	78°C.	79°C.	81°C.	92°C.
in glycerol—water (3:1)	85°C.	87°C.	——	——
†Thickness, in irons	9.6	9.5	9.6	10.1
†Bursting strength, lb. per in. thickness	1250	1300	1220	1300
†Water absorption, %	47.8	47.0	45.9	41.3

*From A, C, and J locations (Fed. Spec. KK-L-311a). All analyses and all physical tests except density, shrink temperature, and bursting strength were made by methods of KK-L-311a.
†Initial values, obtained on butt areas selected for aging tests.

On the third day, the liquor was reheated, its temperature having dropped 20°F. overnight, but no other adjustments were made. Rocking was continued for 2 more days, while the liquors assumed room temperature and their tannin content dropped from 5.35 to 5.0%.

Three sides were retanned separately in a blend consisting of 70% vegetable extracts and 30% lignosulfonate. Here, too, the liquor was 45° Bk. strong, but the pH was lowered only to 3.9. Heat was applied as in the other rocker vats. The length of the retannage was the same so that these sides could be reunited with the others for the subsequent operations.

After rinse-rocking for 1 hr. in water of 120°F., the bellies were cropped off. The backs and bellies were bleached and wrung in the usual manner, oil-wheeled, and loaded separately. Conventional loading materials were employed, except for Orotan, which replaced the imported vegetable extract. Only 2.5% of the syntan on the wrung weight was employed. In order to raise the pH of the leather above 3, an addition of 1% of anhydrous sodium acetate on the wrung weight was given. The oil was reduced to 1¼% on the wrung weight in order to compensate for the greater softness to be expected as a result of the aldehyde pretannage. All subsequent operations were conventional.

ANALYSES AND TESTS

The leathers were analyzed and tested, with the results reported in Table II. All the tests except for density, bursting strength, and shrink temperature were made by the methods prescribed by Federal Specifications KK-L-311a. Density was obtained by dividing the weight of the die-cut specimens for compressibility by their volume before compression. The burst figures were obtained with the 1/8″ plunger (6) on a converted Mullen Tester. Correct shrinkage figures were obtained only after soaking ¼″-wide strips of leather for 16 hours in individual test tubes while applying a vacuum. Water absorption was determined on 6″ x 1″ specimens by allowing them to dry out in a conditioned room between each of the 3 half-hour immersions of which the test consisted. Table II shows only the percentage of water absorbed during the first immersion, since the subsequent immersions did not cause the figures to rise materially. In some instances, they even declined somewhat.

RESULTS AND DISCUSSION

Probably the most remarkable property of the finished leather was its flexibility, which is on the order of the flexible-type sole leather currently in demand. Color and appearance of the grain are rated good by experienced tanners. No drawing and wrinkling was evident in the bend area, and only a relatively small amount in the flanks and shoulder region. Most of the figures for chemical and physical data, shown in Table II, conform to accepted standards for sole leather. Compressibility, for instance, is near 10%. The exception is the low degree of tannage for the leather produced with purely domestic materials. Many investigations in the past have

indicated that high degrees of tannage are, as a rule, unobtainable (4, 5, 7) with lignosulfonate alone even under optimum conditions. When the blend containing only 30% of lignosulfonate was used, the degree of tannage rose a full 14 points, accompanied by a marked increase in density. However, as demonstrated in laboratory tests, the degree of tannage can easily be raised with lignosulfonate alone. A value of 64 has been reached by strengthening the rocker vat on the third day to 80° Bk. By comparison, the blending of more syntan (Orotan) with the unfractionated type of lignosulfonate usually employed for loading was less effective. In the leather the composition of which is reported in Table II, the small percentage of the syntan that was used cannot have raised the degree of tannage more than 2.8%.

Another difference between the group retanned with lignosulfonate alone and the sides retanned with a blend is apparent in the higher water absorption of the former. However, as Table II shows, this difference between the matched sides (c) and (d) was no more than 10%.

On the other hand, the water absorption was higher by comparison with conventional tannages, which confirms observations by earlier workers (8, 9). Since all soles for military footwear have to be oil-treated (10), it was of interest to observe the effect of this treatment on the water absorption. We found that a pickup of about 12% of a commercial product suitable for this treatment resulted in lowering the water absorption to about 15%, which is within the range for conventional sole leather.

The claims that have been advanced for the oil treatment mentioned were of a modest nature as far as longer service of treated soles is concerned (11). Impregnation of soles with blends of polyisobutylene or butyl rubber and resin is said to extend wear much longer (12). These treatments were developed by the National Bureau of Standards for crusted stock only, because finished sole leather ordinarily is too dense for an effective impregnation. We have found that this is not the case with the leather tanned by the new process, using lignosulfonate as the only rocker material. Impregnations were carried out on pieces or cut soles, which gained 15 to 35% in weight after immersion for 1 hour in solutions of different resins like those derived from southern pine wood. One of these, Vinsol*, which is insoluble in the petroleum solvents customarily used, could be dissolved in tetrahydrofurfuryl alcohol, except for a very small residue. After impregnation with these resins water absorption was drastically and permanently reduced, but the flexibility was not affected.

For the stability of leather in storage, no two properties are more important than resistance to thermal shrinkage and fiber strength. In the past, sole leather has been studied for aging effects under favorable conditions, as in cool warehouses (13), but not under conditions closely corresponding to various environments in which leather footwear would be stored

*Hercules Powder Company

for issue to military personnel. Such warehouse conditions simulating three different climates have been created in the climatic chambers of the Quartermaster Research & Engineering Center (14).

Specimens of the sole leather represented by the figures of Table II have already been stored in these climatic chambers. Initially, as can be seen in Table II, the shrinkage temperature in water of the fully domestic leather was approximately 80°C. and was 7°–8°C. higher in the presence of 75% glycerin. This difference recalls recent observations (15) that the Ts of chrome leather in pure glycerin was 12°–22°C. higher than in water. With conventionally tanned vegetable leather the difference is more modest; the regular product of the factory where the tannery trials took place had a Ts of 92°C. by the glycerin-water method prescribed by Federal Specification KK-L-311a, and a Ts of 90°C. in plain water. Evidently Ts measurements in the glycerin-water mixture do not reflect the true heat resistance of any kind of leather, although the increases in Ts in presence of glycerin differ from tannage to tannage. Proper wetting-back of heavy leather presents additional difficulties. Since the Federal Specification is not, as a rule, applied to sole leather, it does not suggest that these pitfalls exist. Once an effective method of wetting finished sole leather had been found, the results obtained were consistent. Table II shows that increasing the quantity of lignosulfonate in the rocker from 30 to 100% caused a marked decline of the Ts in water. By comparison, the small differences in Ts among the beamhouse treatments are probably without significance. Neither did the beamhouse treatments seem to influence the other chemical and physical properties listed in Table II.

Aldehyde-tanned and vegetable-retanned sole leather produced in earlier tannery trials has been retested after one year in the storage chambers. The tannages in question have been described in the report mentioned earlier (2). Regular sole leather obtained from two different tanneries was aged under the same conditions.

The results for bursting strength are compiled in Table III. Most of the leathers showed moderate to large gains. Since 16 specimens were tested before and 16 after aging, and since the distances between the test sites were only about 1 inch, it seemed highly improbable that the strength increases could be attributed to positional variations. In order to prove this point, an analysis of variance was conducted. The F values, also shown in Table III, indicate a high degree of probability that most gains in strength are indeed "real"; statistically insignificant gains and losses occurred only with a few leather specimens aged under temperate summer conditions and with all 5 aldehyde leathers aged in the tropical chamber. Interestingly, the 3 leathers of tannery B lost significantly in strength under desert conditions. Other trends, especially differences among the various aldehydes used, may appear after more extended storage. Observations showing that

TABLE III

BURSTING STRENGTHS OF HEAVY LEATHERS BEFORE (1) AND AFTER (2) STORAGE FOR ONE YEAR

(Bursting strength, lb. per in. thickness)

Test No.	Tannery	Aldehyde Used before Vegetable Retannage	Storage Conditions: Temperate Summer (1)	(2)	Gain %	F Value	Moist Tropical (1)	(2)	Gain %	F Value	Moderate Desert (1)	(2)	Gain %	F Value
1	A	None	1400	1900	36	69.0	1500	1680	12	10.2	1430	1970	38	6.8
2	B	None	1280	1590	24	42.9					1500	1300	−13	18.9
3	B*	None	1590	1600	1	0.3†					1460	1280	−12	8.5
4	B*	Formaldehyde	1640	1800	10	2.2†					1560	1480	− 5	13.3
5	C	Formaldehyde (1a)‡	1320	1630	23	87.9	1420	1460	3	0.3†	1240	1530	23	33.3
6	C	Glyoxal (1b)	1350	1510	12	13.0	1210	1310	8	2.6†	1290	1440	12	7.2
7	C	Glyoxal (5)	1340	1490	11	10.2	1280	1340	5	1.7†	1290	1490	16	36.3
8	C	Glutaraldehyde (3a)	1290	1270	−2	0.2†	1220	1250	2	0.4†	1300	1540	8	56.8
9	C	Oxystarch (4)	1290	1560	21	39.3	1240	1280	3	2.9†	1470	1580	7	6.7

*Used a vegetable extract blended with so-called spruce extract.
†Not statistically significant. The significant level of F is 7.6 at the 99% level and 5.6 at the 97.5% level (30 degrees of freedom).
‡Figures in parentheses refer to experiments reported in Reference 2, Table XIII. As noted there, the stock for experiments 1a and 1b, and for 3a and 5 respectively, consisted of matched pairs of bends. The bends that matched those used in experiment 4 were used in an experiment not reported in the above table.

maximum strength may not be reached for some time after leather has been finished have been reported previously, for instance by Stather and Herfeld (13).

CONCLUSIONS

The unusual emphasis on shrinkage properties of vegetable leather may not appear to be an important point to many tanners. However, military footwear is sometimes stored for years before issue, and, during this time, vegetable soles can suffer losses in shrinkage resistance which are considerable (16). Therefore, leather that possesses a low Ts to begin with may, on occasion, not stand up in use after storage, especially when storage conditions have been particularly unfavorable. It is also well known that lignosulfonate alone cannot materially raise the Ts of untanned hide. Therefore a retanning blend containing lignosulfonate will cause a greater drop in the shrinkage temperature of the aldehyde-tanned leather than a blend containing no lignosulfonate. We found that a blend containing 30% lignosulfonate lowered the Ts of the aldehyde-tanned leather by about 5°C. However, the Ts of the aldehyde tannage is so high that the decline in Ts resulting from the use of lignosulfonate in the retan can be tolerated. Even if lignosulfonate only is employed in the retannage, to the exclusion of vegetable tannins, the Ts of the final leather is still near 80°C., and by varying the proportion of lignosulfonate in the retannage blend the hydrothermal stability can be tailored to suit the requirements and wishes of the user. It is worth noting that conventional methods for facilitating the rapid entry of such blends into heavy hides, for instance by pretreatment with sodium metaphosphate (17), would not have the same effect as aldehyde pretannage in raising the shrink temperature.

For reaching the high Ts desirable at the outset, glyoxal was preferred to formaldehyde mainly because it requires less care in handling; probably it also is less likely to cause a drawn grain. These advantages appear to justify the higher expense of using glyoxal, which in fact, by the standards of the tanning industry, is a low-priced chemical.

The practical benefits of the new tanning process may be summed up as follows:

1. The tanning process is speeded up, requiring no more than 7–8 days from the dehairing to the bleaching operations.

2. The resulting sole leather represents the flexible type which is so much in demand today.

3. The number of rockers needed is drastically reduced and layaways are entirely eliminated. Hence, changes and readjustments, if necessary, are greatly simplified.

4. The cheapness of lignosulfonate compensates for the cost of the pretannage.

5. The number of hides in the process of being tanned and the extract requirements are smaller, resulting in considerable savings.

6. Because no liquors are weaker than 42° Bk., laboratory control work is less complicated.

The findings in this report are presented before final evaluation of the leathers in shoes, in order to give the tanner an opportunity to familiarize himself with the process in peacetime and to adapt it to present needs. This is expected to aid in demonstrating the feasibility of the process and to make it available in case of an emergency when reliance on domestic materials becomes imperative.

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DISCUSSION

A. N. Kay (Howes Leather Company, Inc.): I always feel privileged to be asked to lead the discussion of what I may term a "practical" paper, for the ultimate purpose of all our studies is to help the tanner make better and cheaper leather more quickly. Unfortunately, though of understandable necessity, the results of most of our practical work cannot be published, and it is usually only when someone like the Q.M.C. or one of our suppliers tackles such problems that we have the opportunity of equating in public our science with practical leather-making. The excellent paper we have just heard is one such opportunity, and I hope we will make the most of it.

Those of us who have had the privilege of studying the earlier report referred to, realize very clearly that the deceptively casual simplicity of the present work is the result not of happy chance but of a tremendous amount of careful experimentation and study. In addition to the aldehydes listed in Table II many others were investigated, with and without vegetable, chrome, and zirconium retannages. Perhaps more important is that the conditions required for proper leathering (as distinct from mere combination) were also worked out. The success obtained is clearly evident in the data here presented and, what is more important, in the leather available for inspection. It is not surprising that the leather has such a delightful flexibility; conventional leather, analyzing 45–50% hide substance, would be equally flexible and show an equally high water absorption. What is surprising and important, I feel, is the low compressibility figure.

The work can be criticized on the grounds that the leather will not meet Federal specifications. To the extent that the water absorption is far too high, such criticism has a certain validity, but as Dr. Seligsberger has shown, such leather would be a "natural" for impregnation treatments.

The inability to meet the chemical specifications merely points up the dilemma facing the user and producer of sole leather. Lacking a reliable laboratory performance test, as the Bureau of Standards and the Q.M.C. are the first to admit, chemical testing (plus water absorption and compressibility) is the only way we now have of maintaining quality, and the specification limits are necessarily based on those obtained on good-quality conventional sole leather. If these leathers perform as well as might be inferred from the compressibility figures—and I hope Dr. Seligsberger will publish the performance results as soon as they become available—I have little doubt that provision will be made in the specifications to accommodate this type of tannage.

It is interesting to note that Dr. Seligsberger finds that lignosulfonates lower the shrink temperature. In blends with conventional materials one has tended—at least I have—to assume that this is largely due to a sort of "dilution" effect combined with the lack of "bridging" characteristic of lignosulfonates. Yet, here we have the same effect on an already stable tannage and one which is about as close to being covalent as one could hope for.

There is some evidence that, while lignosulfonates (in conventional tannage) do not fix in great amount, that quantity which is, is fixed very firmly indeed. Is it possible that the lignosulfonate has some special power of stripping off even covalently fixed tanning agents? I wonder if Dr. Seligsberger has any thoughts on this?

DR. SELIGSBERGER: I don't think there is any stripping off of covalently fixed formaldehyde. As we know, the formaldehyde leather does not have to contain even 1½ or 2% to shrink at 88° to 90°. It is remarkable that the smallest amount of formaldehyde will produce a shrink temperature so high. So I do not think the lowering of the shrink temperature is a stripping effect. It is rather a combined effect of two tannages which, we find, sometimes increases and sometimes lowers the shrinkage of the final leather.

L. M. WHITMORE (Leas & McVitty, Inc.): This is a very interesting piece of work, and I think the results on lignosulfonate indicate the usual trend. There is a distinct limit to the degree of tannage you can get with lignosulfonates. You have a hatrack, so to speak, and a lot of small molecules hanging on there, rather than the high-tannin polymers. It is a "natural" for impregnating work, where you are not interested in the high degree of tannage. You get the results of wear and whatever characteristics you want without the high degree of tannage. In the past, the high degree of tannage has been necessary, and probably in this case the blending of even more vegetable tannin with lignosulfonate would be satisfactory.

DR. SHU-TUNG TU (United Shoe Machinery Corporation): I would like to ask Dr. Seligsberger why he uses glyoxal in combination with formaldehyde. What is the advantage of introducing glyoxal, since formaldehyde is much cheaper? Is there anything that formaldehyde would not do alone?

DR. SELIGSBERGER: The main reason was that we had the impression that the glyoxal leather is fuller. Glyoxal is a slightly bigger molecule. Also, the color is not pure white, and a pure white color is not exactly what the sole leather tanner is used to.

DR. TU: Of course glyoxal is a bifunctional aldehyde, besides having a larger molecule. Does the bifunctionality have anything to do with the later treatment?

DR. SELIGSBERGER: I don't think so.

LIFE LINES

Brief Biographies of Our Contributors

HUBERTINA D. CLAYTON—See the February 1958 issue of *JALCA*.

F. G. CONNICK has been employed by the Research Laboratories of Swift and Company in Chicago ever since graduation from the University of Arizona in 1951.

CHARLES W. MANN, a frequent contributor to this Journal, is a graduate of George Washington University. In 1941 he began working for the U. S. Department of Agriculture on hides, tanning materials and leather. Five years later he joined the staff of the Bureau of Standards where he worked for two years on the properties of leather, with emphasis on military leathers. In 1948 he joined the Quartermaster Research and Development Division as head of the Leather Section; now he is Chief of the Leather, Footwear and Handwear Branch of the Textile, Clothing & Footwear Division, Quartermaster Research and Development Command.

DR. LUDWIG SELIGSBERGER, born and educated in Germany, worked both there and in Turkey before coming to the United States in 1937. After many years as chief chemist of the New Castle Specialty Division of Allied Kid Company in Wilmington, Delaware, he joined the Leather Technology Laboratory Branch of the Quartermaster Research and Engineering Center, Natick, Mass., where he is now Chief of the Synthetic Tanning Evaluation Section. He has published several papers in this Journal.

DR. ELDON J. STRANDINE—See the December 1957 issue of *JALCA*.

To Give Leather the Smell of Russia Leather. Extract dry birch bark with alcohol. Distil off the alcohol, pulverize the remaining resin, mix it with 3 parts of calcium hydrate, and distil. The oil passing over soon changes into a resin possessing an aromatic odor like that of Russia leather, and dissolves easily in oils and alcohol.
—*The Techno-Chemical Receipt Book.* Philadelphia: Henry Carey Baird & Co., 1903.

To Protect Fur against the Attacks of Moths. Mix with the liquor used for tanning a mixture of ¼ part rectified oil of turpentine, ¼ of weak solution of carbonate of soda, and 1 of somewhat concentrated decoction of wormwood, and proceed as usual. These proportions are calculated for 100 small skins. For 100 calf or lamb-skins, they being larger, take oil of turpentine 2 pounds, soda-lye 4 pounds, and 8 pounds of wormwood decoction.
—*The Techno-Chemical Receipt Book.* Philadelphia: Henry Carey Baird & Co., 1903.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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EMPLOYMENT

LEATHER CHEMIST WANTED in New England factory for processing inner soles and chrome tanning. Send reply to Box J-600, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

NEW APPOINTMENT

Nopco Chemical Canada Ltd. recently announced the appointment of John D. Tomlinson as General Sales Manager for all Canada. Mr. Tomlinson is an active member of ALCA which he joined in 1955.

DIRECTORY CHANGES

NEW MEMBERS

Joseph C. Barry, 75 Vine Street, Woonsocket, Rhode Island.
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Fred Klimpl, 607 Avenue A, Bayonne, New Jersey.
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R. L. Melton, 507 Seventh Street South, Grand Haven, Michigan.
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Abraham Turow, 1466 E. 21st Street, Brooklyn, New York.
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Jungschlaeger's Quick Process of Tanning. The green hides are placed in a solution of water-glass of 4° to 5° Beaumé, and worked in it from time to time until the hair can be removed. They are then placed in a solution of 2 parts of alum, 0.6 of common salt, a like quantity of sulphate of copper, and 0.2 of sulphate of zinc in 100 of water. During the 5 days the skins are allowed to remain in this solution it is concentrated more and more, and finally brought into the most concentrated form, consisting of 10 parts of alum, 3 each of common salt and sulphate of copper, and 1 of sulphate of zinc. The skins remain for 8 days in this last solution, are then dried at 70° to 85° F., and saturated with tallow, stearine, etc., at 95° to 110° F. The oiled skins are now brought into a solution of soap compounded with soda, in order to fix the metallic salts and to partly saponify the fat. They are finally finished in the same manner as tanned leather.
—*The Techno-Chemical Receipt Book.* Philadelphia: Henry Carey Baird & Co., 1903.

ABSTRACTS

The Chemistry of the Tannins of Spruce Bark. IV. Horst Endres, *Das Leder*, **8**, 222–29 (1957).—Early work on the structure of spruce bark tannin is reviewed (39 references). During World War II spruce bark supplied over 70% of the vegetable tannin used in Germany. The tannin content of 11–12% can be much increased by extraction with sulfite, indicating that the outer bark contains a large amount of high-molecular, insoluble tannin. Inner bark contains soluble tannin that is changed to the insoluble form by enzymes. Enzyme action can be stopped by poisons such as H_2S, SO_2, or HCN. Recent work has used chromatographic methods and solubility fractionation. Kotasek (abstr. *JALCA*, **52**, 594 [1957]) found galacturonic acid, arabinose, glucose, galactose, and probably xylose and rhamnose in the alcohol-acetone precipitate from an aqueous extract of bark. Prchal (in the Max Plank Institute where the present work was done) extracted fresh inner bark, preserved with SO_2, with ethyl acetate, alcohol, and water in that order and obtained the following data:

Solvent	Yield %	Purity	Tan Value	Combining Value	Tanning Action
Ethyl acetate	12.6	80.1	60	7	insufficient
Alcohol	12.7	39.1	69	42	good
Water	17.0	57.9	54	37	very good

Tests with Br_2 and HCHO–HCl indicated a catechol-type tannin; there was no evidence of a pyrogallol type. Only recently have crystalline products been obtained. Inner bark, which contained 17–21% tannin (dry basis), was first extracted with $CHCl_3$ to remove resin, then with ethyl acetate to give 10-15% (bark basis) of an almost colorless tannin mixture having a purity of 80–89. It was a glucoside containing 30% glucose. The sugar could be removed with enzymes; acid altered the aglucon. By column chromatography the following 5 fractions were separated from the glucoside: A, 2.1%; B, 3.5%; D, 7.5%; E, 35.0%; and E′, 7.5% (gravimetric determinations). A larger amount of fraction E was separated and crystallized; it contained 54% sugar. The aglucon was also crystalline. On a kieselguhr-cellulose column 2 fractions were obtained from the aglucon, but on a polyamide column, 6 fractions. The fact that a polyamide column retains the aglucon but not the glucoside is being studied for its tanning significance. Aglucon had the empirical formula $C_{15}H_{16-18}O_5$. Preparation of several derivatives showed that all 5 of the oxygens belonged to hydroxyl groups that were esterified; the aglucon was not therefore of the catechol type. The UV spectra of fraction M and catechol also differed. The spectra of aglucons M and E were almost identical with that of 4,4′-dihydroxy-3,3′-dimethoxystilbene, and the IR spectrum was also in agreement with a hydroxystilbene structure. The iodine number and hydrogenation of derivatives show there is a double bond. All 5 hydroxyl groups of fraction M were aromatic in nature. In the glucoside 2 of the hydroxyls were each coupled with a molecule of glucose because reaction with diazomethane or fluorodinitrobenzene produced trimethoxy or tri-dinitrophenyl glucoside respectively, but after splitting off sugar the 2 remaining hydroxyl groups reacted with these reagents. By paper chromatography

on an ethyl acetate extract of inner bark 5 spots were found that corresponded with 5 of the 21 reported by Lindstedt and Zacharias in an acetone extract of a commercial spruce extract. The results in general show that over 50% of the ethyl acetate–soluble portion of inner spruce bark is not of the catechol tannin type. I.D.C.

Outline of the Preparation of Aromatic Syntans. I. Raw Materials and Basic Operations. G. Reich. *Das Leder*, **8**, 229–37 (1957).—A review with 60 references. The most important source of information regarding preparation of syntans is the patent literature; there are many more than 1000 patents. The most important raw material is ordinary phenol. The supply and price are quite variable in different countries; much is produced by synthesis, but it has numerous uses other than in the manufacture of syntans. Catechol and its homologs are outstanding materials for synthesizing tannins and produce materials nearly like vegetable tannins. The condensation product of catechol and HCHO is soluble in water without sulfonation and tans well but is too costly. Catechol is found in variable amounts in brown coal, and the crude distillation product is sold in Germany as "Brenzöl" and in Czechoslovakia as Diphen or Optol. Naphthalene is used for dispersing or auxiliary syntans. The naphthols, dihydroxydiarylsulfones, and dihydroxydiphenylpropane are important raw materials. Ligninsulfonic acids are abundant and cheap and are used in various states of purity or modification as dispersing or tanning agents. Condensation is needed because the simple hydroxyaryls do not tan; they cause hide to swell. Coupling of at least 2 aromatic rings and the presence of at least 2 reactive points of attachment far enough apart are required if the syntan is to link together polypeptide chains and tan. Tanning ability increases with increasing number of points of affinity and also with increasing molecular size until the molecule is so large that there is steric hindrance. Condensation involves several kinds of coupling or bridging. The sulfodepside bridge, $-SO_2-O-$, is of historical interest only. The sulfonimid bridge, $-SO_2-NH-$, has limited use; the best known example of its use is in Tanigan supra LL which is expensive but valuable because of the white, light-stable leather which it makes. The sulfone bridge, $-SO_2-$, has long been known in dihydroxydiarylsulfones. In the formation of 4,4′-dihydroxydiphenylsulfone from *p*-phenolsulfonic acid and phenol the former can be completely condensed if an excess (2–3 mols) of phenol is used. Low pressure greatly favors the reaction and decreases resinification. The excess of phenol can be distilled off as an azeotropic mixture with the water of reaction. Condensation at 170° C. for 50 hr. gave a 92.5% yield; at 145° for 10 hr. a 75% yield; and if a longer column was used and the temperature raised to 196° there was a 95–97% yield in 4 hr. The methylene bridge is of great technical importance for linking 2 nuclei. The use of HCHO for this purpose is found in the pioneer work of Stiasny. With acid or alkaline condensing agents HCHO and hydroxyaryls form the very reactive methylol compounds such as phenolalcohol ($OHC_6H_4CH_2OH$). With acid condensing agents the phenolalcohols react at once with unreacted hydroxyaryl to form compounds with 2 or more rings united by methylene bridges. Further condensation results principally in linear products. Mixtures of these poly ring compounds, if soluble in alkaline-aqueous solution or in alcohol, are known as novolaks. With alkaline condensing agents 2-ring compounds are formed which contain additional methylol groups and these then can condense to form a 3-dimensional network.

Formaldehyde, at suitable pH values, not only causes an increase in particle size of the condensate but also increases its solubility because of formation of hydrophylic compounds. Most syntans must be made soluble in water; the introduction of hydrophilic groups, however, reduces tanning ability, so a compromise must be made between solubility and tanning action. Solubility may be obtained by sulfonation with H_2SO_4, by sulfomethylation with HCHO and sulfite or bisulfite, or by amphoterization with aldehydes and amines. These 3 methods of solubilization are the basis of a proposed system for classifying sytans. **II. The Manufacture of Sulfonated, Methylsulfonated, and Amphoteric Syntans.** G. Reich. *Ibid.*, **9**, 6–15 (1958).—A review with 57 references. There are 3 types of sulfonated syntans. In one the aromatic material is first sulfonated, then condensed with HCHO to form auxiliary tannins that tan only below pH 2 but speed tanning and prevent formation of sludge. If phenol or cresol are sulfonated at 110° C. with an equal (mol basis) amount of H_2SO_4, 20–25% will remain unsulfonated. During condensation this unsulfonated portion will condense preferentially to form an insoluble novolak and the whole mixture may gel. Naphthalene is usually sulfonated with an excess of acid, and as acid speeds condensation, it may be necessary to remove this excess acid. The reaction of naphthalene and HCHO is slow under some conditions but is more rapid with methylolurea. In another type of sulfonated syntan novolaks are sulfonated to form high-quality exchange syntans that are suitable for light but not normally for heavy leather. Sulfonation should be moderate with not more than 1 sulfo group per 2 phenolic rings. Ligninsulfonate liquors can be mixed with these syntans. The novolak may be made, for example, either by dissolving phenol in HCHO and then adding acid slowly (the reaction is violent) or by dissolving phenol in acid and water then adding the HCHO. The third type of sulfonated syntan is made by condensing a mixture of sulfonated and unsulfonated hydroxyaryls with HCHO. This process is the most important because it can be varied to make tanning materials suitable for different types of leather. Catechol, as the unsulfonated component, makes a syntan that produces soft leather; dihydroxydiphenylsulfone, firm; and phenol, medium firm. Sulfonated naphthalene or naphthol results in flexible, but ligninsulfonic acid in very firm, leather. Sulfomethylation or ω-sulfonation is of less practical importance but is used in mixed condensations. Amphoteric syntans, $(C_6H_4OHCH_2C_6H_4OHCH_2H_2NR)Cl$, are soluble in acid as substituted NH_4 salts and in alkali as phenolates. Their tanning ability increases as the proportion of basic component (amine) decreases. When used alone at low pH they give a weak, rapid tannage that is intensified by later raising of pH. Some types produce soft, unusually full leather with good dyeing properties. Refining syntans for use involves purification from mineral acids and salts, adjustment to a suitable pH value, and if a granular form is desired, drying. Mixed condensates made with alkali contain large amounts of salt which can be removed by pouring the hot syntan into a 35–40%, acidified solution of $(NH_4)_2SO_4$ and centrifuging or pressing out the precipitated tannin. In this process Na salts are changed to NH_4 salts. Acid-condensed products need no purification by salting out, but if too much acid is present, it can be removed with lime. If ligninsulfonate is used, Fe and Ca must be removed either before it is used or from the finished syntan. All aromatic syntans except auxiliary are adjusted to pH values of about 3.2–4.2 with NH_4OH or organic acid. In many cases 5–15% (tannin basis) of organic acid is added to buffer the hide during tanning. This acid increases the purity found by analysis. Syntan extracts, which usually contain between 40 and 60%

water, can be converted to the solid form by spray- or drum-drying, by evaporation, or by special methods such as the worm press. It is possible to hold the amount of water to a minimum during condensation by the use of concentrated aldehydes, gaseous NH_3 for neutralization, etc. Syntans are used (1) to augment the supply of vegetable tannins in times of emergency, (2) to compensate for disadvantages of vegetable tannins, and (3) to produce entirely new effects.
I.D.C.

Precipitation of Sulfur as Barium Sulfate in the Presence of Orthophosphate Ions. K. R. Kar and N. Nath. *J. Sci. Ind. Research* (India), **16B**, 563–66 (1957); *Chem. Abstr.*, **52**, 9852*h*.

Rapid Determination of Alkali Bicarbonates in the Presence of Alkali Carbonates with a Precipitation Procedure: L. Szekeres and E. Bakacs. *Z. Anal. Chem.*, **159**, 414–18 (1958); *Chem. Abstr.*, **52**, 9865*a*.

Structure of Collagen Chains. M. I. Millionova and N. S. Andreeva. *Biophysics* (U.S.S.R.), **2**, 292–99 (1957) (English translation); *Chem. Abstr.*, **52**, 10251*g*.

Structure of Elastin. I. Analysis of Some Acid Peptides. A. Kärkelä and E. Kulonen. *Acta Chem. Scand.*, **11**, 1434–35 (1957) (in English); *Chem. Abstr.*, **52**, 10259*e*.

Periodic Deformation of Collagen in Solutions of Electrolytes and Tanning Agents. A. G. Pasynskii and A. M. Tongur. *Colloid J.* (U.S.S.R.), **19**, 483–88 (1957) (English translation); *Chem. Abstr.*, **52**, 10621*f*.

Chromatography of Amino Acids on Sulfonated Polystyrene Resins. An Improved System. S. Moore, D. H. Spackman, and W. H. Stein. *Anal. Chem.*, **30**, 1185–90 (1958). **Automatic Recording Apparatus for Use in the Chromatography of Amino Acids.** D. H. Spackman, W. H. Stein, and S. Moore. *Ibid.*, 1190–1206. H.B.M.

Titration of Weak Bases in Strong Salt Solutions. F. E. Critchfield and J. B. Johnson. *Anal. Chem.*, **30**, 1247–49 (1958).—Weak bases with ionization constants as low as 1×10^{-11} can be titrated with indicators in 6 to 8*M* solutions of neutral salts. Potentiometric titrations can be applied to bases with ionization constants as low as 1×10^{-12}. H.B.M.

Chinese Gallotannin. H. G. C. King and T. White. *Chem. and Ind.*, **1958**, 683–84; *see also JALCA*, **53**, 189–90 (1958).—The suggestion that Chinese gallotannin may be of a galloylated tri- or tetrasaccharide, rather than penta-*m*-

digalloyl glucose cannot be substantiated. Glucose is the only carbohydrate obtained from this tannin by acid, alkaline, or enzyme hydrolysis. However, other data are not in agreement with the classical structure wherein *m*-digalloyl residues are joined esterwise to glucose. Further investigations are in progress.
H.B.M.

The Behavior of Hide Powders from Different Sources for the Quantitative Determination of Tannin. Report of the Tannin Working Group of the Union of Swiss Leather Chemists. W. Weber, Reporter. *Das Leder*, **9**, 61–63 (1958).—Three laboratories using chestnut and cold-soluble quebracho extracts or syntans compared Freiberg, Lyon, Darmstadt, and Vienna hide powders; each laboratory, however, used a different procedure. They conclude that Darmstadt powder No. 87 can be considered satisfactory. It gave the same tannin value with Gerbstoff Marken C and F as Freiberg powder but 2–3% lower values with 3 other syntans. There was very good agreement in the results with 4 different lots of Freiberg powder. All 4 white hide powders gave good results when chromed and used in the Darmstadt apparatus, although Darmstadt powder GB 11 and Lyon powder lot 9 swelled too much. All were suitable for the international shake method. All 4 prechromed powders removed tannin completely in the filter method. Freiberg powder was best, then the Darmstadt powder. With chestnut wood extract and increasing amounts (from 2.0 to 4.5 g. per 50 ml. of tannin solution) of either prechromed or white hide powder essentially constant tannin values were obtained except for increasing values with chromed Lyon powder. With quebracho extract the results with different powders were variable possibly because of the higher pH value (5.4) of this extract.
I.D.C.

The Preparation of Water-soluble Leather-oiling Materials by Addition of Bisulfite to Unsaturated Oils. II. The Sulfiting of Sperm Oil. A. Küntzel and L. K. Schwörzer. *Das Leder*, **9**, 49–55 (1958); *see JALCA*, **52**, 644.—The source and properties of sperm oil are briefly described. Sperm oil is difficult to sulfite because of its low iodine number (82–92) and its high content (30–40%) of unsaponifiable matter. On treating 200 g. of oil with 100 g. of 40% bisulfite solution at 65°–75°C., a water-in-oil emulsion formed in 2 hr., but this changed in 10 hr. to an oil-in-water emulsion. The optimum reaction time was 15 hr.; after 20 hr. the emulsion deteriorated. If heated to 100°C. for a short time the emulsion separated into a clear unemulsified upper layer and a yellow emulsified lower layer (25% of the total) that formed stable emulsions with either sperm oil or the upper-layer oil. Altering conditions such as the proportion of bisulfite to oil, time, or temperature did not improve the product. Sulfiting in methanol was tested by heating 200 g. of oil, 100 g. of bisulfite, and 150 g. of methanol under reflux with aeration for 15 hr. at 65°C. The product separated in a few days into emulsion and oil layers and solid Glauber's salt; however, if the product was poured at once into water, a stable emulsion was formed. Although the use of methanol had some advantages, it increased work, time, and cost. Emulsions were not formed in a high-pressure autoclave in tests at various temperatures and pressures; during pressure-sulfiting there was extensive saponification and the free fatty acids that were liberated had no emulsifying properties. Since the raw oil could not be sulfited successfully,

fractionation of the oil was attempted. Freezing did not give a separation, so the method of Kaufmann and Kirsch (*Fette und Seifen*, **49**, 841 [1942]) was used. Both cod and sperm oils were fractionated by dissolving the oil in acetone and holding for 24 hr. at —17°C. For cod oil only a small amount of acetone was needed, but for sperm oil a ratio of oil to acetone of 1:5 was required to give a satisfactory separation. The liquid fraction from cod oil had a higher discrepance (75–81) (discrepance is the difference between the iodine and thiocyanogen numbers) than the solid fraction (27–41), but for sperm oil the reverse was true. The values were 8–16 for the liquid sperm oil fraction and 15–21 for the solid fraction; the unsaturated fatty acids of sperm oil are mostly C_{12}–C_{16} acids. The solid sperm and the liquid cod oil fractions were sulfited. Sperm oil could be sulfited satisfactorily if the discrepance was 15 or more, but it was necessary to adjust the amount of bisulfite downwards according to the discrepance. The solid fraction of sperm oil (iodine number 87, discrepance 21) was sulfited under reflux at 70°–75°C. with 35 g. of fresh 40% bisulfite solution using cobalt resinate (0.1% Co) as catalyst, 5% of sulfited sperm oil as emulsifier, and regulating air flow to 1 bubble per 3–4 seconds. After 6 hr. the reflux condenser was removed, and heating continued for about 5 hr. until a clear product was obtained. The facts that oils with high discrepance are better for sulfiting and that the amount of sulfite must be adjusted to the discrepance were confirmed with linseed, cottonseed, and coconut oils. The stability of sulfited and sulfated (with sulfuric acid) sperm, cod, and cottonseed oils was tested by treating 20-ml. portions of 10% emulsions of these oils with 3 ml. of the following solutions: 5% $CaCl_2$, $FeSO_4$, or alum; 20% HCl, 20% sulfited quebracho, or a chrome liquor containing 13.8 g. Cr_2O_3 per l. The emulsions of sulfated oils became cloudy or precipitated at once, as they contained much free fatty acid. The sulfited cod and sperm oils formed quite stable emulsions unless the medium was strongly acid. Sulfited cottonseed oil emulsions broke in 6 hr. after adding alum or chrome solutions, but this instability was caused by salting out and could be reversed by adding water. Salting out was limited to sulfited oils having not more than 2 unsaturated bonds per molecule. Sulfited sperm oil was more stable to acid than sulfited cod oil because of its low triglyceride content and is therefore more suitable for chrome leather. I.D.C.

Industrial Wastes Effects at South San Francisco, California, Sewage Treatment Plant. H. L. Schweining. *Sewage and Ind. Wastes*, **29**, 1377 (1957).—The million-dollar South San Francisco–San Bruno sewage treatment plant is described. It has a designed capacity of 8 mgd with a peak of 13 mgd, and municipal and industrial wastes can be kept separate or treated together because all the equipment is in duplicate. The pretreatment units consist of automatic bar screens, two grit chambers with straight-line grit collectors, and a screw conveyor to the grit hoppers. There are 4 flocculation tanks and 4 primary sedimentation tanks; the latter are equipped with sludge collectors and pipe skimmers. Raw sludge is drawn by gravity to either of 2 sludge thickening wells and pumped to the digesters. There are 2 70-ft. primary digesters equipped with floating covers and heated by 2 sludge heaters. Industrial wastes come from three meat-processing plants and a packing house, a tannery (chrome process), a steel-pickling plant, and a shop-towel laundry service. The treatment plant receives all the tannery (Poetsch and Peterson) wastes except the chrome

and hair wastes. Plans for a pretreatment plant for the treatment of chrome wastes and removal of excess suspended solids have been authorized by the tannery. J.F.W.

Tannery Waste Treatment with Sewage at Williamsport, Pennsylvania. T. R. Haseltine. *Sewage and Ind. Wastes*, **30**, 65 (1958).—The treatment plant is designed to handle a maximum of 500,000 gpd of industrial waste plus the sanitary sewage from an ultimate population of 10,000 people. It incorporates primary treatment and chlorination with vacuum filtration and incineration of the resulting undigested sludge. The tannery waste comes from the Williamsport tannery of Armour Leather Company which has a capacity of 52,000 to 54,000 lb. of hides per day. At capacity the tannery produces about 400,000 gpd of wastes, approximately 75% of which are discharged over a 10-hr. period. The tannery wastes are pumped to the treatment plant through approximately 2,800 ft. of 10-in. and 12-in. pipes by means of 3 quadruplicate plunger pumps taking suction from a wet well. At the treatment plant the wastes enter a tannery-waste holding tank which is 70 ft. in diameter and equipped with a mechanical sludge collector but has no overflow weir or fixed liquid level. The tank outlet is situated to allow about 80,000 gal. of liquid storage capacity above and about 60,000 gal. of sludge storage capacity below. This permits the treatment of the tannery wastes at a uniform rate over a 7-day week despite the wide variations in the rates of discharge by the tannery; it also permits the collection of the heaviest tannery solids prior to further treatment. The wastes pass through a flow regulator and Venturi meter and then become mixed with the municipal sewage at either the inlet or outlet of the preaeration tank. Sludge is pumped from the tannery-waste holding tank to primary sedimentation basins. The final sludge is dewatered on 2 coil-type vacuum filters, each of which has an effective area of 150 sq. ft. Belt conveyors receive the filter cake (as well as sewage grit and screenings) and discharge to a hearth incinerator. The municipal sewage reaches the plant through a flow regulator in a combined sewer. At the plant it passes through a mechanically cleaned bar screen and a retention-type grit chamber to a wet well, from which it is pumped to a preaeration tank. The preaeration tank is of the spiral-flow type equipped with spargers and has a theoretical detention time of 48 min. at an average flow of 1.1 mgd. There are two rectangular sedimentation basins equipped with conventional chain and flight sludge collection and skimming mechanisms. Together these tanks theoretically afford a 2.7-hr. retention period, a surface settling rate of 740 gpd/sq. ft., and an overflow weir rate of 10,600 gpd/ft based on an average flow of 1.1 mgd. The effluent is chlorinated and then flows to the Susquehanna River. Provision in design will permit installation of a secondary treatment process. Complete operational data for the period May 1956 through April 1957 are tabulated. The average monthly reduction in BOD was 54% and the reduction in settlable solids, 13.7%. From the sludge recovery data a solids recovery of 71.6% is noted. The most serious problem encountered has been the concentration and filtration of the sludge. It is desired to have sludge contain at least 6 to 7% of solids, and considerable experimental work was necessary to achieve this. A procedure was finally developed that is giving from 8 to 10% solids and entails careful pumping of the sludge and removal of the supernatant liquid from the holding tanks daily. In the discussion of this paper by F. E. Heller, Secretary of the Williamsport

Sanitary Authority, the economic considerations and operating costs of this treatment plant are described. J.F.W.

The Effect of Beamhouse Operations on the Character of Pig Upper Leather. F. Stather, H. Herfeld, and H. Moser. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.*, **No. 11**, 3–34 (1955).—Results are given for a series of 28 test lots (20 skins each) in which the effects of changes in the liming, degreasing, or bating processes were studied by comparison with a standard procedure. All lots were Cr- tanned alike, and part of each lot was finished for suede and part for full-grain leather. The leathers were analyzed for fat at several stages, subjected to physical tests, and appraised subjectively for quality. In the standard procedure the skins were soaked 24 hr., fleshed, limed for 8 hr. with 200% water and 8% Na_2S crystals at 30°–25°C., washed, relimed for 4 days with a white lime, washed, delimed with $(NH_4)_2SO_4$, washed, refleshed, degreased with 2.5% Desapon A and 0.1% NaOH, washed, and bated with $(NH_4)_2SO_4$ and 1% Pellucit O. Bristle removal was unsatisfactory with 6% or 4% Na_2S when liming was started at 30°C.; with 3% Na_2S at 36°C.; in and 4- or 5-day lime with 2–4% Na_2S plus lime; and in a 17-day white lime. Weight yield was improved by omitting reliming and worsened by prolonged liming with $Ca(OH)_2$ only. Both these changes lowered the area yield. The strength of the leather was decreased when the initial liming temperature exceeded 30°C. and when liming was prolonged; it was improved when reliming was omitted and when the painting process was employed. Loose leather resulted from high-temperature liming, prolonged liming, and doubling the quantity of bate. Omission of reliming made the leather too firm. The character of the grain was improved by using the painting process, by shortening the liming process, and by prolonging the bate. The above applies to full-grain leather. The character of pig suede was improved by a more drastic liming, either by use of higher temperature or by extending the time in the relime. The average fat content of the skins after fleshing was 9.4, 10.9, and 11.7% (on hide substance) in butt, shoulder, and belly respectively. About 54% of the fat was removed in liming (less when reliming was omitted or shortened), 3% in deliming, 10% in the degreasing operation, and 3% in bating, leaving about 30% of the initial fat in the bated skins. Addition of degreasing agent or NaOH to the soak was not beneficial. The degreasing operation was less effective when done before liming, before reliming, or before deliming. Five other commercial detergents were tried instead of Desapon A, with no appreciable effect on degreasing or leather quality. H.B.M.

The Influence of Retanning, Neutralization, Fatliquoring, and Finishing on the Properties of Corrected Grain Pig Upper Leather ("Kona" Leather). F. Stather, H. Herfeld, H. Moser, and K. Härtewig. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.*, **No. 12**, 3–30 (1955).—The leather in question is buffed and given a plated finish, either smooth or with an artificial grain. The main purpose of this work was to prevent the reappearance of typical pigskin grain when the leather is stretched, as in lasting. Vegetable retannage accomplishes this by making the leather firmer and less stretchy. Tests with a variety of natural tannins and syntans showed that natural tannins, e.g., pine bark extract, give the firmest and least stretchy

leathers, and certain syntans the softest and most stretchy, although these differences can be equalized to some extent by varying the quantity of fatliquor. About 4% pure tannin on the shaved weight should be given. The skins should be buffed deeply to remove all the grain layer, preferably before vegetable retanning, using a coarse paper first, followed by a very fine paper. This can be accomplished by a procedure analogous to the common process for suede (neutralizing, partially fatliquoring, drying, buffing, and then wetting back, dyeing, fatliquoring, and retanning) or more economically by doing the coarse buffing on the damp skins in the blue and the fine buffing after the skins have been tacked out, or even after the first finish coat. The leather should be neutralized thoroughly and fatliquored before retanning, otherwise the uptake of fat will be incomplete and variable. Finishing is done by applying 2 coats by swab and 2 by spray, using a blend of protein and synthetic binders (Eukanols). The proportion of synthetic to protein binder should be 2 : 1 to attain adequate extensibility of the film before cracking occurs (about 30%) and adequate resistance to flex-cracking. Application of the bottom coats at high dilution is advisable. The finished leather is rather impervious to passage of air or liquid water, but permeability to water vapor is considered adequate.

H.B.M.

The Most Suitable Tannage and Retannage for Pig Suede Leather. H. Herfeld, F. Stather, K. Härtewig, and H. Moser. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.*, **No. 12**, 31–55 (1955).—The authors tanned 25 test lots (15 skins each), all processed alike through the beamhouse by the standard procedure described above. In the standard tanning procedure the skins were pickled with 8% NaCl and 1.0% H_2SO_4 in 200% water; tanned in the spent pickle with 3% Cr_2O_3 ("Basochrome"), half added at 33% and half at 50% basicity; neutralized to 50% over-all basicity; piled, wrung, split and shaved; neutralized with 2.5% Na_2CO_3; partially fatliquored, dried, damped, staked, and tacked out; buffed flesh and grain and brushed; wet back with 1% Pekorol LM in 1000% water at 60°C.; retanned with 3% Cr_2O_3 (Cr alum) on the dry weight, half the liquor being adjusted to 33% and half to 50% basicity with Na_2CO_3; neutralized; retanned with lightly sulfited quebracho equal to 1% pure tannin; washed, dyed, and fatliquored. In the 24 experimental lots the tanning and/or retanning conditions were altered, and the resulting leathers were compared with the standard with respect to subjective properties and physical tests. It was found advantageous to tan at higher basicity by lowering the pickle acid to 0.5% and feeding all the Cr liquor at 42% basicity. This resulted in a higher Cr content, better fat takeup, improved measurement yield, and better subjective qualities. These improvements were obtained, but to a lesser degree, by increasing the temperature during tanning. Omitting the vegetable retan seemed to result in better strength, improved handle and smoothness, but poorer resistance to wetting; this last probably could be overcome by modifying the fatliquor. All other changes were disadvantageous, including tannage with less Cr, "dry" tannage, tannages with liquors variously masked, pretannage with alum, and similar changes in the Cr retannage.

H.B.M.

The Most Suitable Methods for Fatliquoring and Mechanical Finishing of Pig Suede Leather. H. Herfeld, F. Stather, and K. Härtewig. *Ges.*

Abhandl. Deut. Lederinst. Freiberg/Sa., **No. 13**, 3–36 (1956).—The shaved leather was neutralized, fatliquored, dried, damped, staked, tacked, buffed, wet back, retanned, colored, and re-fatliquored. Tests were made using 6 different sulfated oils that varied widely in degree of sulfation, ratio of emulsifier to emulsified fat, and "water absorption number" (*see JALCA*, **51**, 335 [1956]). Test lots were given 3.5% actual fat (on shaved weight) in the first fatliquor, and 0.8% in the second fatliquor. Small lots were fatliquored with 5 different sulfated oils, and each lot was split into 5 sublots that were re-fatliquored with 5 different sulfated oils or mixtures. Contrary to expectations it was not necessary to use a highly sulfated oil in order to secure satisfactory buffing. On the contrary, the leather made with low sulfated oil was superior in most respects but hard to wet back. Best results were obtained with a 1 : 2 mixture of high and low sulfated oils. Further tests showed that best results were obtained with the application of 2.5–3.0% actual oil (on shaved weight) in the first fatliquor, and 1.0% in the second. Results of numerous tests of mechanical treatments are reported. Drying should be done at not over 30°–35°C., and the leather should be toggled under slight tension. All the grain layer should be buffed off, but the grain should not be buffed too deep, otherwise the pig characteristics become evident. A complete process for making pig suede leather is given, summarizing the results of this series of papers. H.B.M.

Pigment Finishing of Pig Upper Leather with Corrected Grain ("Kona Leather") Using Synthetic Binders. F. Stather, H. Herfeld, K. Härtewig, and H. Moser. *Ges. Abhandl. Deut. Lederinst. Freiberg/Sa.*, **No. 13**, 37–68 (1956).—The application of commercial synthetic resin finishes is discussed. The following general conclusions are drawn from the results of many experiments: Use of fats with too high a water absorption number is bad, because then the first finish coat soaks in too much. The ground coat should be a straight synthetic resin of a high degree of softness. The succeeding coats (one or two plush coats and one or two spray coats) should be combinations of protein and synthetic resin so formulated that the softness decreases from the under to the upper coats. (This should be attained by using the right proportions of harder and softer binders rather than varying the amounts of plasticizer added.) The final glaze coat should be straight protein binder. The temperature and pressure of the plating press must depend on the thermoplasticity of the individual coats. It is suggested that the leather be smooth-plated after the ground coat, embossed with a fine pattern after the plush and spray coats, and finally smooth-plated after glazing. The embossing is then scarcely noticeable but serves to hide the pig grain. Emphasis is placed on securing the right degree of fixation of the finish coats. H.B.M.

Pigskin and Pig Leather. F. Stather. *Das Leder*, **9**, 35–39 (1958).—An address summarizing the author's previously published investigations. H.B.M.

Societal Aspects of Pollution Control. By R. D. Hoak. *A.M.A. Arch. Ind. Health*, **17**, 446 (1958).—Air and water pollution are dissimilar in some respects, but they do have a number of points in common. The most significant

correspondence between the two is the paucity of dependable technical data on the specific effects of particular factors and combinations of factors. The administration of pollution controls is difficult but has often been compounded by unrealistic legislation. In the case of stream pollution abatement the emphasis has been placed on uniform effluent standards, which fail to take into account the volume or quality of the receiving stream. Such standards are gradually being replaced by stream standards, whereby concentrations of specific substances are limited to appropriate value after admixture with the receiving water, thus taking advantage of the assimilative capacity of the streams and utilizing this factor as an economic resource. The vital need for more fundamental research studies on the specific effects of air- and water-borne materials is emphasized. J.F.W.

Screw Drums in Soviet Tanneries and Possibilities of Their Application in Czechoslovakia. M. Spieka. *Kozarstvi*, **7**, 68–70 (1957); cf. *JALCA*, **52**, 43 (1957).—These screw drums are very long horizontal cylinders, divided into compartments by a continuous helical partition. Skins enter the first compartment and are advanced to succeeding compartments by turning the drum through 360°. Agitation is affected by rocking through 170°–220°. Such drums are being used for soaking and liming, and for vegetable retanning. The technology of bating, deliming, pickling, and chrome tanning in screw drums is still under development. For liming, the drum is 16 m. long, divided into 7 sections, the first for soaking and the other 6 for lime liquors. Volume of the individual sections increases from 9.1 for the first to 11.5 cu. m. for the last section, with useful capacities of 4.5 to 5.75 cu. m. A charge of 1250 to 1500 kg. green weight of hides is fed to the first section, washed for 30 min. with 200–300% water, drained, and soaked 5 hr. at 27°–29°. The charge is then advanced to the next section, where it is limed with a liquor containing 15–18 g. CaO and 0.6–0.7 g. Na_2S per l. at 32°–34° C. At regular intervals a new charge enters the soak compartment, and the skins being limed are advanced one compartment. The whole soaking-liming cycle takes 36 hr. The hair is conserved. This process cuts the requirement for floor space per ton of hides per day to 24 sq. m. compared to 36 sq. m. for pit-liming. Productivity is doubled because of reduced manual handling. The screw drum for vegetable retanning is 30 m. long, 2.5 m. in diameter, and has 30 sections. The charge is 500–600 kg. of prechromed pelts in 200% float, so that the whole apparatus holds about 15–18 tons of hides and about 30 cu. m. liquor. The first 16 sections correspond to a rocker section, the 17th to 26th sections to retan drums, and the 27th to 30th sections to wash drums. The wash liquor is fed back to an earlier section. The spent liquor from the first section contains 0.2–0.6% tannin. The concentration of tannin in the 15th section is 5.5–6.0%. Fresh extract containing 20% tannin is fed to sections 17 and 18, and the concentration falls in section 25. Advantages and disadvantages are discussed. L.M.

Building and Location of Tanneries. L. Masner. *Kozarstvi*, **7**, 20–22 (1957).—The annual capacity of new unit U.S.S.R. tanneries is given as 3,000 tons sole leather, 100 million sq. dm. Cr upper leather, and 90 million sq. dm. of Cr–vegetable retan heavy upper leather. These tanneries are combined with shoe factories for 4.5 to 6 million pairs of shoes. About half the hand work in

older tanneries is really internal transportation. Mechanization, using 5-ton overhead cranes, and the new screw-type drums (*see* preceding abstract) is recommended. The former BATA tannery units, with daily capacities of 400 steerhides, 800 calfskins, and 100 goatskins, are too small to use highly productive machines to best advantage. The productivity of a new Czech sole leather tannery at Otrokovice is given as 50 hides per week per worker, compared to alleged outputs of 41, 34, and 24 hides per week for 3 named U.S. tanneries. Corrosion of tan pits was studied. Concrete pits should be lined with ceramic tile. Painting with alcoholic phenol-formaldehyde resins has given poor results, and lining with polyvinyl chloride is unsuitable if temperatures exceeding 45° C. are to be encountered. Tannery wastes, after removal of 80–90% of suspended matter by sedimentation, may be discharged directly into a stream, providing that the resulting dilution is at least 200 to 1 on at least 350 days out of the year; otherwise chemical or biological purification is necessary. Cold, sterile well water is best for soaking and liming, and soft, filtered river water is perhaps best for other operations. Water consumption is 4000% of fresh weight of hides for sole leather tanneries, and 8000% for upper leather tanneries. L.M.

Brush Dyeing of Glove Leathers. O. Zajicek and J. Turecek. *Kozarstvi*, **7**, 6–7 (1957).—The leather is brush-dyed on small palettes of phenol-formaldehyde resin carried by a conveyor. Each worker performs only one operation so that differences in shade have largely been eliminated. L.M.

An Apparatus for the Determination of Shrinkage Temperature and the Degree of Shrinkage of Leather. V. Oplustil. *Kozarstvi*, **7**, 31–32 (1957).—A sample 60 x 100 mm. is immersed horizontally in water and attached to a lever which operates directly on a dial that shows the percentage of shrinkage. A second apparatus provides 5 levers and 5 dials. L.M.

Synthetic Rubbers as Raw Materials for Shoe Cements. A. Kolinsky. *Kozarstvi*, **7**, 14–16 (1957).—The following formula is given: chloroprene rubber (cold-polymerized) 100; MgO 4; ZnO 5; antioxidant 2; modified colophony or synthetic resin 5–30; fillers 0–50 parts. The resin is an essential component, as the chloroprene rubber has very little adhesion by itself. A hydrogenated or disproportioned colophony may be used, or various synthetic resins. The optimum ratio of resin to rubber is 15–50 to 100. Nitrile rubbers or high styrene-butadiene rubbers may also be used. These cements may be used also for attaching polyvinyl chloride soles to shoes. An addition of 33% of 5–10% Desmodur R in CH_2Cl_2 is recommended. These cements are used wet or activated with acetone. L.M.

Substitution Reactions of Reinecke's Salt. A. A. Adamson. *J. Am. Chem. Soc.*, **80**, 3183–89 (1958); cf. Gustavson, *JALCA*, **53**, 192–202 (1958).—The (NCS) groups of $Cr(NH_3)_2(NCS)_4$ are displaced successively by solvent molecules. Rate of solvolysis is about the same in water and methanol, and much slower in nitromethane. Ammonia is not displaced. The reaction kinetics are discussed. H.B.M.

The Mechanism of Action of Elastase. V. Moret and L. Gotte. *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat.*, **23,** 442–47 (1957); *Chem. Abstr.*, **52,** 11134*d*.

The Intrafibrillar Network Structure of Collagen. E. Kuhnke. *Naturwissenschaften*, **44,** 509–10 (1957); *Chem. Abstr.*, **52,** 11135*a*.

Transformation of Collagen to Elastin in Dermal Collagens with Varying Sensitivity toward Collagenase. M. K. Keech. *Ann. Rheumatic Diseases*, **17,** 23–50 (1958); *Chem. Abstr.*, **52,** 11156*h*.

Treatment of Trade-Waste Waters and Prevention of River Pollution. P. C. G. Isaac, ed. *Univ. Durham-King's Coll. Dept. Civil Eng.* **Bull. No. 10,** 312 pp. (1957); *Chem. Abstr.*, **52,** 11325*g*.

The Tannins of Sprucewood Bark. W. Grassmann, G. Deffner, E. Schuster, and W. Pauckner. *Chem. Ber.*, **89,** 2523–35 (1956); *Chem. Abstr.*, **51,** 8091*f*. **III. Chromatographic Separation of Tannins on a Polyamide Column. Isolation of a Second Aglycon from Sprucewood Bark Tannin.** W. Grassmann, H. Endres, W. Pauckner, and H. Mathes. *Ibid.*, **90,** 1125–28 (1957); *Chem. Abstr.*, **52,** 11413*d*.

Sulfur Fat Tanning. I. Binding Sulfur with Collagen in the Process of Sulfur Tanning. R. Dzieza. *Prace Inst. Przemysl Skorz.*, **1956,** No. 1, 77 pp.; *Chem. Abstr.*, **52,** 11451*b*.

The Effect on Shoe Leather Water Absorbability of Multiple Soaking and Drying. E. Raabe and M. Witanowski. *Przeglad Skorzany*, **1956,** No. 9, 221–24; *Chem. Abstr.*, **52,** 11451*h*.

Aging of Finished Leather. J. Drezner. *Przeglad Skorzany*, **1956,** No. 2, 1–4; *Chem. Abstr.*, **52,** 11452*b*.

Studies on Picking Band Leather. S. Sen, N. Dasgupta, and A. Chakraborty. *J. Indian Leather Technologists' Assoc.*, **New vol.,** No. 1, 34–39 (1958).—Tensile strength measurements and microscopic examination of raw, limed, pickled, tanned, dried, and stuffed hides indicate that high tensile strength is associated with low weave angle and medium to high degree of splitting up of fibers. Uniformity of vertical distribution of Cr and stuffing grease increases with degree of fiber splitting. H.B.M.

A Method for Evaluation of Organic Sulfur in Commercial Waste Sulfite Liquor. K. B. Mathur and S. K. Barat. *Bull. Central Leather Research Inst., Madras*, **4,** 296–307 (1958).—Knowledge of the organic sulfur content of commercial lignosulfonate is desirable if the lignosulfonate is to be used for tanning, either directly or after chemical modification. The material analyzed

was a mixed Ca–Mg lignosulfonate, 72% solids, pH 7.5; at that pH value no SO_2 or bisulfite could be present. Organic sulfur is determined by subtracting the sum of sulfate and sulfite sulfur from the total sulfur. Total sulfur is best determined by wet oxidation with HNO_3 and $HClO_4$ followed by precipitation as $BaSO_4$ (Salvesen and Hogan, *Anal. Chem.*, **20,** 909 [1948]). Sulfate is determined by a modification of the conductimetric titration method of Peniston *et al.* (*Anal Chem.*, **19,** 332 [1947]). The raw lignosulfonate is diluted with 1 to 2 parts water, and a 10 ml. aliquot is put through a column of Amberlite IR-120 in the sodium cycle to replace Ca and Mg by Na. The effluent and washings are diluted with an equal volume of isopropyl alcohol, and titrated conductimetrically with 0.5*N* $BaCl_2$. The end point corresponding to complete precipitation of $BaSO_4$ is marked by a sharp increase in the slope of the graph of $BaCl_2$ vs. conductivity. Sulfite is determined by the T.A.P.P.I. iodimetric method. H.B.M.

Manufacture of Fancy Leathers from Chrome-tanned Grain Leathers and Splits. A. Ganesan. *Bull. Central Leather Research Inst., Madras,* **4,** 308–12 (1958).—Procedures are given for application of decalomania and for hand color block printing. H.B.M.

Production of White Leather. V. Pektor and J. Ondracek. *Kozarstvi,* **7,** 287–97, 306–11 (1957).—A review. Both Al and HCHO tannages are used only in combination with other tannages. Tannages described are: (1) Bleached Cr tannage on goatskins, with 1.7% Cr_2O_3, best neutralized with 5% $Na_2S_2O_3$ in 200% water at 30°C.; bleached with 0.5% oxalic acid and 10% of a bleaching syntan in 300% water at 45°C. for 45 min.; and fatliquored with 3% sulfated castor oil in 200% water at 55°C. for 45 min. European bleaching syntans are rated in the order: Irgatan RLB, Biltan 1115 (experimental), Kortamol NNO (Czech), Basyntan FC, Albatan (Hungary), Tamol NNO, and 2 experimental syntans. (2) Sulfochloride tannage; pretannage with 0.4–0.6% HCHO (100%) at pH 7.7–7.9, 2 hr. at 20°–22°C., followed by horsing 12 hr.; wringing to 55% water; tanning with 14–16% sulfochloride (on wrung weight) and 4.2–4.8% Na_2CO_3 at 42°–47°C. exactly, for 60–80 min.; drying for 3 days at 40°–47°C. to exactly 11–14% water; staking; drumming 20–30 min. in 800% water (on dry weight) at 45°C.; adjustment to pH 7.7–8.3 by Na_2CO_3 (about 0.2%) and 80–90 min. further drumming, followed by washing 25–35 min. at 40°–45°C.; fatliquoring with a maximum of 3% sulfated castor oil (on dry weight) plus 2% white pigment and 0.05% blue casein color. Retannage with Cr makes this leather more elastic and easier to finish. (3) Melamine tannage; pickling with 8% NaCl, 1% H_2SO_4 and 100% water; tannage in 30% of spent pickle plus 70% water to which is added 8% melamine dissolved in 50% spent pickle, boiled, and cooled; drumming for 4 hr. with pH adjustment to 3.8–4.1 every 30 min.; left in drum overnight, run 20 min., horsed 24 hr., then fatliquored. Pretannage with 5% Cr alum in 70% water and 30% spent pickle is also possible. (4) Zr tannage. Formulas for nitrocellulose and casein-resin binder finishes with white pigments are given; casein-resin is preferred. Three grindings of the pigments are necessary. L.M.

The Determination and Fractionation of Sulfates in Water Solutions of Chrome Alum. A. Blazej and A. Mracna. *Koza stvi,* **7,** 324–28

(1957).—The determination of total sulfate, free SO_4 ions, and cold- and warm-titrated acid SO_4 ions was studied. Total SO_4 ions are determined gravimetrically by precipitation with benzidine dichloride. Cold and warm titrations were made with phenolphthalein. Cold titration determines free H_2SO_4, SO_4 ions bound electrovalently to cationic Cr, and part of the coordinately bound SO_4. During the potentiometric titration with antimony or glass electrode, points of inflection occur at pH 3.3 and 8.5; the former corresponds to titration of free H_2SO_4. Solutions with pH under 2.8 always contain free H_2SO_4, those with pH 2.8 to 3.3 sometimes do, and those with pH over 3.3 never do. Titration of the boiling solution gives both ionic and complexly bound SO_4. L.M.

Testing of Leather Dyestuffs. B. Niewieczerzal. *Kozarstvi*, **7**, 346–48 (1957).—Development of dyes for leather is described. Their testing has not yet been standardized. Some companies use a blue scale with 8 shades as in the textile indutry; Bayer modified it; others use 5 shades. Sandoz (Basle) compares the dyes to be tested with reference dyes by dyeing leather samples. This procedure is used in U.S.S.R. Different tests are not comparable. Poland uses the Sandoz system, limited to 6 shades as no dye has been found with a higher resistance to light. Dyed samples of leathers and textiles cannot be compared as textiles bleach out while leathers change color. Washing resistance is measured in the textile industry by 3 standards, but although dyed leather samples often bleed in water or by washing, they are not colored by the dye that is bled out. Textile methods cannot therefore be used with leather. The Sandoz method for measuring penetration by examining fresh cuts gives qualitative results. A Swiss method to determine levelling properties of dyes by dyeing leather with different dye concentrations (1 to 10%) has been recommended. Spotting on filter paper is useful. Chromatography of dyes on leather (Vrbacky, abstr. *JALCA*, **52**, 528 [1957]) is mentioned. L.M.

The Control of Washing and Deliming Pelts. A. Blazej and E. Markusovska. *Kozarstvi*, **7**, 357–59 (1957).—Limed pelt contains 2–6% CaO on the dry basis. Of the CaO present initially, 72, 61, 37, 31, and 29% is still present after washing for 0.5, 1, 2, 4, and 8 hr. The lime present in skin can be classified as water-soluble, partly soluble Ca salts of amino acids, and Ca bound insolubly by COOH groups of proteins. Control of lime content by spotting with phenolphthalein is only qualitative. The colorimetric method of Stehlik (Abstr. *JALCA*, **52**, 405 [1957]) applies only to a narrow range of Ca concentrations, and the colored compound is too unstable for the preparation of standards. A chelametric method employing Komplexon III (the disodium salt of ethylenediamine tetraacetic acid) is proposed. Cut a strip about 1x2–3 cm. from the butt, weigh to 0.01 g., transfer to a 250-ml. Erlenmeyer flask, and hydrolyze by boiling with 30 ml. *N* HCl. Add 50 ml. redistilled water, neutralize to methyl orange with 2*N* NaOH, and add 2 ml. of 2*N* NaOH and 10 ml. of a buffer solution containing 2 g. NH_4Cl and 100 ml. conc. NH_4OH per 1. Add 0.3 g. Murexide (NH_4 salt of purpuric acid), and titrate with 0.01*M* Komplexon III (3.721 g. per 1.) to the change from reddish orange to blue-violet. The hydrolyzed collagen does not interfere in amounts up to 1.5 g. nitrogen in the sample. Analyses of limed steerhide gave the following percentages of CaO on the dry basis, the

differences being the maximum for 5 replicates: limed 2.80–2.85; washed 2.01–2.12; delimed 1.61–1.64; bated 1.15–1.19; and pickled 0.28–0.35.

L.M.

Chemical Studies on the Hair. I. Sulfur-containing Amino Acids Especially on Lanthionine. M. Funatsu and M. Kikutani. *Nippon Nogei -Kagaku Kaishi*, **30**, 572–76 (1956); *Chem. Abstr.*, **52**, 12000c.

Sedimentation and Diffusion of α- and β-Components of Procollagen and Their Ratio. V. N. Oreckhovich, V. O. Shpikiter, and V. T. Vaslavskii. *Biokhimiya*, **23**, 285–90 (1958); *Chem. Abstr.*, **52**, 12005*g*.

Avens as Tannin-bearing Plants. K. F. Blinova. *Sbornik Nauch. Trudov Leningrad. Khim.-Farm. Inst.* **2**, 80–90 (1957); *Referat. Zhur. Khim., Biol. Khim.*, **1958**, Abstr. No. 3362; *Chem. Abstr.*, **52**, 12099*d*.

A Laboratory Screening Test of Bactericides for Use in Sheep-Pelt Soaking Pits. J. H. Richardson. *Appl. Microbiol.*, **6**, 142–45 (1958); *Chem. Abstr.*, **52**, 12437*h*.

Tannins. VII. Colorimetric Determination of *d*-Catechol in Catechu. K. Kimura, Y. Satomi, and S. Kuwano. *Yakugaku Zasshi*, **78**, 325–29 (1958); *Chem. Abstr.*, **52**, 12439*a*.

Elastin. II. Mucopolysaccharides in Elastin Fibers. L. Gotte and V. Moret. *Atti Accad. Naz. Lincei Rend. Class Sci. Fis. Mat. Nat.*, **23**, 281–86 (1957); *Chem. Abstr.*, **52**, 12940c.

A Collagen-like Compound Isolated from Bovine Spinal Fluid. I. E. Roboz, N. Henderson, and M. W. Kies. *J. Neurochem.*, **2**, 254–60 (1958); *Chem. Abstr.*, **52**, 12947*g*.

Investigation of Tanning Characteristics of *Rhododendron Aureum*. P. D. Sokolov. *Botan. Zhur.* **43**, 437–43 (1958); *Chem. Abstr.*, **52**, 13295*f*.

Chromatography of the Sulfonated Products of Phenol– Formaldehyde Condensation. I. Paper Chromatography of Phenolsulfonic Acids. E. Mück, D. Kokes, and F. Langmaier. *Chem. Listy*, **52**, 746–48 (1958); *Chem. Abstr.*, **52**, 13295*f*.

Determination of the Degree of Sulfitation of Vegetable Tanning Extracts. A Stehlik, D. Kokes, M. Podolska, and E. Mück. *Veda a Vyzkum v Prumyslu Kozedelnem*, **2**, 53–8 (1957).—The procedures of Turley *et al.* (*JALCA*, **36**, 329–37 [1941]) are considered too long. The following procedure is offered for determining free SO_2, SO_2 present as sulfite, and SO_2 bound to tannin. *Free SO_2:* Dissolve 50 g. of solid sulfited extract in 1000 ml. water (cold), adjust the pH to 2.8–3.1 by adding HCl, pipet 50 ml. of the solution into a 250-ml. flask, boil under reflux in an atmosphere of N_2 for 1 hr., and distil into a 3% solution of H_2O_2. Titrate the acid formed by oxidation of the distilled SO_2 with 0.1*N* NaOH, to the bromphenol blue end point. *SO_2 combined with tannin:* To the residual solution in the flask add 5 ml. conc. HCl and 10

ml. HCHO (40%), boil under reflux 30 min., cool, filter the precipitated tannin, and wash with hot water to a negative reaction with $BaCl_2$. Colloidal precipitates obtained with highly sulfited extracts can be filtered hot after adding 10% potassium acetate solution to the suspension. Transfer the washed precipitate to a Kjeldahl flask, oxidize to a transparent solution by adding 5 ml. fuming HNO_3 and 80 ml. H_2O_2, and determine sulfate gravimetrically. A blank test with nonsulfited quebracho is run to correct for SO_4 in the reagents, particularly H_2O_2. Lignosulfonate, if present, must be removed before the analysis by adding 1 g. urea and filtering. Sulfited quebracho extracts contained 3.28 to 3.72%, and sulfited spruce extract 2.16 to 4.58% of SO_2 combined with tannin. The following percentages of SO_2 combined with tannin were found in spruce extracts sulfited as indicated:

% $NaHSO_3$ used	0.6	0.9	none	none	none
% Na_2SO_3 used	0.6	0.9	2.0	3.0	5.0
% SO_2 combined with tannin	2.28	2.96	2.16	3.36	4.58

L.M.

Experience with Drying of Pasted Side Upper Leather. V. Pektor and L. Hula. *Veda a Vyzkum v Prumyslu Kozedelnem*, **3**, 99–188 (1958).—The hygroscopic equilibrium in the drying of pasted side upper leather has been determined. Medium liming and short, intensive bating are recommended. It is stated that "foreign" side upper leathers contain 3% Cr_2O_3 and 7.5% fat. The amount of fat given in the fatliquor should be 15–20% higher than for nonpasted leather, and at least 20% of the fat must be nonsulfated. A recommended fatliquor contains sulfated oil (containing mineral oil) 3.0–4.0, nonsulfated rapeseed or neatsfoot oil 1.3–1.6, and surface-active agent 0.5–0.7%. The pH of the cut should be 4.5–5.0 after neutralization. Drumming for 35–40 min. in fatliquor is necessary. For retanning after fatliquoring, a mixture of 60% wattle extract and 40% Syntan SN_{25} is recommended. A recommended paste contains 2.0–2.5% potato starch, 90–95% water extract from sunflower cake, and up to 5% sulfated oil. The leather before pasting should contain 55–60% water. The recommended cycle for drying side leather is: 2 hr. at 45°C. and 60% R.H., 5 hr. at 55° and 50% R.H. to 30–33% water, 1 hr. at 55° and 40% R.H., and 1 hr. "conditioning" at 45° and 55% R.H. Drying of other types of leather is also described. The final water content should be 15%. The dried leather is conditioned for at least 6 days at 18°–20°C. and 65% R.H. The area gain for side leather is 5–6, for pig shoe upper 6–8, for horse upper or garment 10–12, and for box calf and kid (only partly dried) 4–5%. L.M.

Utilization of Leather Industry Wastes. C. Halamek, M. Radil, and J. Lacnak. *Kozarstvi*, **7**, 275–78 (1957).—The following percentages of wastes, figured on the fresh weight of the hides, are obtained in Czechoslovakia: hair 2, machine fleshings 24, hand fleshings 4, split fleshings 18, Cr shavings 10, fat 3. Sole leather trimmings amount to 25% and upper leather cuttings 14–16% (of the leather ?). The hide substance is utilized in shoes to the extent of 56% for sole and 26–27% for upper leathers. The best use of sole leather cuttings is

disintegration of the fibers and use in plastic "leather". A large unit for producing this "leather" is under construction. Alkali-hydrolyzed sole leather cuttings can be used for mordanting wool. Their use in fertilizers is economically unsound; the cost of their nitrogen is three times that of commercial fertilizers, and acid hydrolysis before use in fertilizers is too expensive. Attempts to detan the cuttings with NH_3, recover the tannin, and use the protein for feedstuffs, also proved uneconomical. Dry distillation of the cuttings has been tried. (Kashpin, Moscow: Vsesoyuznoe kooperat. izdatelstvo, 1954). Other suggested uses are for "cementing" (case-hardening ?) steel, polishing metals, and production of activated carbon. Urbanek (Leather & Allied Trades Research Inst., Gottwaldov, Czech.) has isolated amino acids and peptones from sole leather cuttings. At present the most economical use of large quantities of sole leather cuttings is to burn them; their calorific value is about equal to soft coal. A medium-quality glue is produced commercially from Cr shavings and Cr leather trimmings. Cr shavings are used mostly in plastic "leather". A feedstuff is produced commercially in Otrokovice by acid hydrolysis of Cr leather trimmings. A plant for producting this feedstuff by pressure hydrolysis is under construction and should be more efficient economically. The feedstuff contains 43.13% proteins and 39.51 nonprotein nitrogen-containing materials. Of the nitrogen-containing materials, 82.2% are edible. The Cr_2O_3 content is only 0.04%. This feedstuff has been used successfully for feeding pigs, replacing 5% of the total protein fed, and replacing imported fish meal. Split fleshings are used for artificial casings and, along with other fleshings, for glue and gelatins of various grades. L.M.

Shellac for the Final Dressing of Shoes. G. Rojcik. *Kozarstvi*, **7**, 63–66 (1957).—A good shoe dressing must form a clear, plastic film that does not become hard and brittle on aging. It must have good wetting properties and a pH value up to 8.5. Dressings are tested for gloss (Lange glossmeter), pH, wetting properties, adhesion, flexibility, permanence of gloss, and viscosity in °Engler. The specifications for the shellac used are: *scales*, ash 0.07, water 1.0, acid no. 76, saponification value 207, insoluble in alcohol 0.08%; *bleached*, ash 0.1, water 27.0, acid no. 65, saponification value 236, insoluble in alcohol 16.2%. No plastic has been found that can entirely replace shellac. Triethanolamine is preferred to borax for dissolving the shellac; it acts as a plasticizer also. A good dressing contains 100 parts ruby scale shellac, triethanolamine equivalent to acid no. 20, 856 parts water, and 10 parts Nigrosine WL. The finish is modified for spongy leathers by adding casein, and for quicker drying by replacement of part of the water by alcohol. Nigrosine WL should contain about 35% ash, pH of a 2% solution 8.2, and should have a bluish shade. A colorless dressing should contain about 13–15% solids, pH 7.5–8.5, vicosity 1.1°–1.5° Engler for normal leathers and 1.5°–1.8° for spongy leathers. A black dressing contains 14–16% solids, pH 7.5–8.5, viscosity 1.2°–1.5°. The shellac is dissolved in water containing triethanolamine at 70°–80°C. The nigrosine is dissolved separately and added to the finish, which is filtered and allowed to mature for several days. *p*-Cl-*m*-cresol is recommended as preservative. Application of the dressing is best made by a fine-textured sponge, 2 coats, with complete drying between coats. L.M.

Pickle Variations. Fritz Kähne. *Das Leder*, **9**, 135–37 (1958).—A pickle adjusts the pH of the skin to that of the chrome liquor so that the skin will

not take up acid and make the liquor too basic. A normal pickle consists of water 100%, salt 8%, and sulfuric acid 1% on the skin white weight. In order to prevent swelling, the salt concentration in the liquor must be 6° Bé. after the skins have been added. A float of 80–100% in a tan drum may be used, but if this causes drawn grain, a paddle and a 500% float should be used. The pH of the solution should be between 2 and 4, usually between 3.2 and 3.6. After pickling, the skins should be well drained because flat leather will result if too much salt is carried over into the tan liquor. Masking agents may be added to the pickle. Sulfate has a mild masking action, but chloride has none. A HCl pickle makes flat, firm leather with a good grain. Non-swelling acids, such as Decaltal N (sulfophthalic acid) or N powder, can be used without salt. The skins should be thoroughly pickled throughout; light-weight material can be pickled in 1 or 2 hr. but unsplit cattlehides should be left in the pickle overnight. Pickling is a safe way to hold skins without damage. I.D.C.

Development of Pigmented Casein Finishes. L. Blazek. *Kozarstvi*, **7**, 215–17 (1957).—Plasticizers for casein and their effects on the quality of the finish have been studied. A sulforicinoleate containing 3.9% organic SO_3 softens well and gives a translucent solution. Use of 75 to 100% of this material on the dry casein prevents fixation of casein by HCHO. Glycerol may be added up to 50% of the casein; it does not inhibit HCHO fixation. Triglycol is better than glycerol, giving translucent solutions, and 75 to 100% does not interfere with fixation by HCHO. However, the films shrink a little after 72 hr. at 70°C. Diglycol is more volatile than triglycol, and its films shrink more during heating. The extensibility of good casein films containing 60 to 70% plasticizer is lowered to 18–24% by fixation with HCHO. Addition of pigments, waxes, etc. lowers the extensibility by 30 to 50%. Among replacements for casein, Luron Binder U without plasticizer gives films with extensibilities of 116 and 45% before and after fixation with HCHO. "Calfaplast" with 50% triglycol shows corresponding extensibilities of 60 and 36%. L.M.

Remarks on Steam, Water, and Electrical Energy Consumption in Tanneries. M. Tomisek. *Kozarstvi*, **7**, 311–13 (1957).—The following figures are given:

Kind of leather	Water (liters)	Steam (kg. at 3 atmos.)	Electricity (kw/hr)	Average yield in kg. or dm.²	Raw hide consumption (kg.)
Sole—per kg.	80-120	4.0-5.5	0.25-0.35	0.558 kg.	1.780
Boxcalf—per 10 dm.²	25-35	1.75-2.25	0.06-0.08	21.2 dm.²	0.472
Calf suede "	50-25	2.75-3.25	0.10-0.12	19.5 "	0.512
Glazed kid "	45-50	1.3-1.8	0.06-0.08	31.2*	.....
Side upper "	40-45	2.25-2.70	0.07-0.09	16.8 "	0.595
Pig upper "	25-30	1.5-2.0	0.05-0.07	22.0 "	0.454
Pig nubuck "	40-45	2.3-2.8	0.08-0.10	21.0 "	0.454
All shoe upper " (mean)	40-45	2.0-2.5	0.07-0.09	.....	.....

* dm.² per skin.

L.M.

Impregnation of Leather. L. Masner. *Kozarstvi*, **7**, 168–70 (1957).—A review with 105 references. Topics covered include: impregnation of sole leather by heat-solubilized phlobaphenes of quebracho, the British hotpitting process, dimethylolurea precipitated in the leather by $Al_2(SO_4)_3$ or (better) boric acid, polymerized linseed oil, and plastics; impregnation of gasket leather with liquid polysulfide polymers; impregnation of insole leather with Cr or Al salts, cationic syntans, aminoresins, or Al lignosulfonate; and impregnation of upper leathers with silicones, Al soaps, Nylon, natural or synthetic rubber, Cr stearate, and alkylsuccinic acid condensates. Impregnation by polymers offers several difficulties, as leather often contains negative polymerization catalysts, and polymers of high molecular weight can be incorporated in leather only with difficulty. The best procedure, perhaps, is to impregnate with polymers of low molecular weight and polymerize to a high molecular weight *in situ* by prolonged heating. L.M.

Use of Aminoresins in Tanneries and Their Influence on Mold Growth. E. Pospisil and P. Safarik. *Kozarstvi*, **7**, 93–96 (1957).—Aminoresins are products of the condensation of phenol, HCHO, and NH_4Cl or $(NH_4)_2SO_4$. When aminoresin was used with $Al_2(SO_4)_3$ to impregnate leather, heavy mold growth (*P. glaucum and A. niger*) occurred in the leather dryers. This led to a study of the effects of sole leather loading materials on mold growth. Mold grows freely on $MgSO_4$. Aminoresin in low concentration acts as a N-nutrient for mold growth; in higher concentrations it inhibits growth. Syntans have a variable effect; phenolic syntans restrict mold growth more than naphthalenic. Both aminoresin and $Al_2(SO_4)_3$ react with syntans, liberating OH groups and lowering the mold-inhibiting effect. Molds (*P. glaucum and A. niger*) grow best at pH 3.5–4.5. Addition of *p*-nitrophenol to the impregnating compound is recommended when syntans are not used. L.M.

Influence of Aminoresins on the Resistance of Vegetable-tanned Leather to Sweat. M. Micka. *Kozarstvi*, **7**, 128–30 (1957); *see* Ferebauer, abstr. *JALCA*, **52**, 406 (1957).—Vegetable-tanned insoles, insoles retanned with aminoresin and neutralized, and the same not neutralized, shrank 8.7, 2.2, and 2.3% respectively after immersion for 35 days in artificial sweat. The same types of insoles shrank 14.0, 9.2, and 11.5% respectively after 4 months of wear. Results are not directly comparable with those of Beebe *et al.* (JALCA, **49**, 630 [1954]) as the test method is different. A method was developed for measuring staining of socks by insoles. A piece of white filter paper is sandwiched between the leather specimen and a rubber sponge saturated with artificial sweat, a 100-g. weight is applied, and the assembly is stored at 37°C. (time not stated). Then the paper is dried at 50°C., and its reflectance in amps^{-9} is measured by a Lange photocell and compared with the reflectance of unstained paper. Insoles impregnated with aminoresin showed considerably less staining than ordinary vegetable leather insoles. L.M.

Brief Introduction to the Measurement of Color and the Use Thereof. A. Brockes. *Das Leder*, **9**, 73–81 (1958).—Brief descriptions are given of measurement of transmission and extinction curves, the color triangle,

and spectrophotometric instruments, in particular the Hardy (General Electric), Color-Eye, and Elrepho (Zeiss) instruments. These tools, although costly, are of considerable value in control work. An exact quantitative expression for the difference between two colors is needed: although several color-difference formulas have been proposed, none has yet been adopted internationally.
I.D.C.

New Lines of Development of Air-Permeable Plastic [Imitation] Leather. V. Smejkal. *Kozarstvi*, **7**, 60–61 (1957).—The author holds that the world's production of shoes, stated to be 1,279,000 pairs per annum, and leather clothing points up the need for higher output of plastic (polyvinyl chloride) imitation leather. Air permeability can be imparted by perforation (U.S.); by incorporation of water-soluble salts (NaCl or KCl) which subsequently are leached out (U.S.S.R.), which however lowers the abrasion resistance; or by incorporation of gas-forming salts and subsequent heating. Frescoflex imitation leather is produced in Italy by applying narrow strips of PVC on textiles. The surface is easily soiled. An air-permeable imitation leather is being made in the German "Democratic" Republic by applying only 100 to 150 g. per sq. m. of PVC to combed textiles. Production of air permeability by electrostatic discharge has been described but not used in production so far as known. Plastic imitation leather based on felt is not as yet suitable for shoe uppers. Air permeability is not the only requirement for good imitation leather. It must also possess a sufficient water absorption and the ability to give up water at about 25°C. and 70% relative humidity, as well as the necessary stiffness and elasticity. The water absorption from the grain side should be higher for imitation linings and insoles, but lower for imitation shoe uppers and clothing. Water absorption can be increased by increasing the percentage of textile fibers, by using hydrophilic materials in compounding the PVC plastic, or by developing a new hydrophilic plastic with good abrasion resistance. Low thermal conductivity is also necessary.
L.M.

The Nature of Amino-Formaldehyde Resin Tannages. W. S. Short and G. R. Mittler. *J. Soc. Leather Trades' Chemists*, **42**, 179–90 (1958).—The mechanism of resin tannage with amino resins and in particular with dimethylol urea is discussed. The high shrinkage temperature of leather containing amino resins polymerized "*in situ*" suggests a chemical combination between collagen fiber and resin. High shrinkage temperature of dimethylol urea–treated leather may also be due to liberation of free HCHO which combines with the fibers. Plots of shrinkage temperature vs. pH for dimethylol urea–treated and HCHO-tanned leathers were very similar, as were also the "leatheriness" characteristics of the two types of leathers prepared at similar pH values. In tanning with dimethylol urea, a certain degree of HCHO tannage appears to be essential before resin absorption can occur.
J.M.C.

Studies on Zirconium Tannage. The Ionic Nature of Zirconium in Masked Solutions of Zirconium Sulfate. T. S. Ranganathan and R. Reed. *J. Soc. Leather Trades' Chemists*, **42**, 205–10 (1958). Cf. *JALCA*, **53**, 478 (1958).—Conflicting views exist regarding the ionic state of Zr in solutions of

Zr sulfate. Ion-exchange resin chromatography and paper electrophoresis were used to investigate citrate-masked solutions of Zr sulfate. Addition of citrate to freshly made solutions of Zr sulfate reduces the percentage of Zr in cationic form to zero while increasing the percentage of anionic complexes to as high as 96%. J.M.C.

Chinese Leather Industry. Du Tchouen Yen. *Kozarstvi*, **7**, 130–31 (1957).—Tannin contents of Chinese materials are: bark of "dahuried turczaninow" (larch sp.), 8–10; acorn cup of *Q. serrata*, 11–12; bark of *Picea sikiangensis*, 15–16; leaves of "ven pu" (*Vaccinia utilis*), 21–22; stalks of "chun gen", up to 24; fruits of "chua sjan" (*Platycatia siangensis*), up to 37%. A large factory for extracting larch bark is being built, and factories for extracting *Q. serrata* and "chun gen" are being rebuilt. A short description of Chinese tanneries is given. L.M.

Mongolian Tanneries. R. Batyn. *Kozarstvi*, **7**, 132 (1957).—Mongolia has 30 domestic animals per inhabitant. Of the hides and skins produced, 30% of the sheepskins, 60% of the goatskins, and 50% of the heavy hides are tanned locally. The first Mongolian tannery was started in 1934. Sole leather is tanned with 75% oak wood and 25% willow bark extracts, imported from the U.S.S.R. No syntans are used. Czechoslovakia furnishes tanning machinery and is training Mongolian tanners. L.M.

Damage to Hides by Insects. M. Tomisek. *Kozarstvi*, **7**, 61–63 (1957).—Damage to hides by insects during the life of the animal is said to account for 63% of total hide defects. Damages by *Anoplura*, *Mallophaga*, *Demodices*, and *Acarina* are described. For protection against insects, washing the animals with a 1% solution of DDT or "HCH", or repeated spraying with a suspension of colloidal S in a 7% solution of K soap gives good results. The entire surface of the animal must be covered. L.M.

Evaluation of Shoe Cements. G. Rojcik. *Kozarstvi*, **7**, 157–60 (1957).—Shoe cements are classified as wet-binding, heat-activated, melted thermoplastic, and solvent-activated. Laboratory tests are made to determine initial and slip strength of the joint, and final strength after exposure to O_2 or water for 2 and 24 hr. Methods for static and dynamic testing and an apparatus for measuring the adherence of the cemented sole to the shoe are described. L.M.

Measurement of Heat-insulating Properties of Materials. R. R. Ferebauer. *Veda a Vyzcum v Prumyslu Kozedelnem*, **2**, 27–44 (1957).—A new apparatus for the measurement of heat-insulating properties of shoes is proposed. The insulating properties of leathers and textiles have been determined. The coefficient of heat conduction (K) is defined as gcal. passing through a hexagon having a volume of 1 cc. in 1 sec. at a temperature difference of 1°C. Values of K are: boxcalf, 21.46; side upper, 20.46; vegetable upper, 19.97; and upper and lining leathers in general, 22.45 to 17.41. The apparatus cannot be used for sole leather. L.M.

Shoe Stiffeners. A. Sejkora and Z. Liss. *Kozarstvi*, **7**, 91–93 (1957).—Materials used for stiffeners include nitrocellulose, urea-HCHO resins, and polyvinylbutyral. Thin stiffeners impregnated with nitrocellulose may be softened by alcohol instead of acetone. Urea-HCHO resin stiffeners may be softened by a 1-min. immersion in a saturated solution of NH_4Cl. Polyvinylbutyral stiffeners are used for shoes clicked automatically. These as well as nitrocellulose stiffeners may be softened by exposure to alcohol vapors, and then immersed in an alcohol - acetone mixture (3 or 4 to 1). L.M.

Syntan from Dihydroxyphenols. I. Paper Chromatography of Pyrocatechol. Z. Kotasek. *Veda a Vykum v Prumyslu Kozedelnem*, **2**, 5–11 (1957).—A Novolak was prepared by treating 55 g. pyrocatechol in 50 ml. water with 19 ml. HCHO (40%) and 3 ml. conc.HCl. heating to 50°C. for 10 min., then raising the temperature from 64° to 90°C. and holding at 90°C. for 3 hr. The product was water-soluble. Descending and ascending chromatograms of pyrocatechol were obtained with *n*-butanol saturated with water and CCl_4 (1:9). The chromatograms were dried at 20°C. and developed with 1% solution of ammoniated $AgNO_3$ or with 2% ammonium phosphomolybdate. The R_F value found for pyrocatechol was 0.70 (0.65 to 0.75), in agreement with Mraz' value of 0.67. The R_F values for constituents of the Novolak were 0.60, 0.50, 0.40 and 0.30. L.M.

Principles of Dyeing and Finishing of Leather. V. Pektor and J. Ondracek. *Kozarstvi*, **7**, 225–31 (1957).—A review. Aniline dyes are tested for dyestuff concentration, differences in shade, solubility, pH of 1% solution, and stability toward acids and bases. The pH of the dye bath should be 6.5–7.0 for direct dyes, and the pH of the leather cut before dyeing should be 4.6–4.8. Dyeing of dry suede, nubuck, glove, garment, and vegetable-tanned leathers, the use of various dye assistants, and pigment colors are described. L.M.

Tannin Extract Factories for Spruce Bark. I. Binko. *Veda a Vyzcum v Prumyslu Kozedelnem* (Science and Research in the Leather Industry), **2**, 13–25 (1957).—About 30,000 tons of spruce bark are produced annually in Czechoslovakia, but only 25,000 tons are expected in 1960 and 20,000 tons in 1970 because of planned limitations on deforestation. The economics of the manufacture of spruce bark extract and its suitability for tanning are considered. Recommended are extractors of 15 cu. m. capacity taking a charge of 2 tons of bark and 6 cu. m. of liquid, which shrinks to 3.8 cu. m. after soaking. Extraction at 70° to 90°C. is preferred because pectins are soluble at high temperatures. Sulfite extraction is deprecated. **Influence of Temperature and Chemicals on the Extraction of Spruce Bark, with a Method for the Determination of Pectic Substances and Polysaccharides.** I. Binko, J. Kolar, Z. Pospichalova, and I. Ivanic. *Ibid.*, **2**, 77–87; see also *JALCA*, **52**, 583 (1957).—Extraction with NaOH gives very viscous extracts containing pectins and polysaccharides. The following procedure is recommended for their determination: To 150 ml. of the extract solution add slowly 300 ml. of ethanol denatured with ether, separate the precipitate by centrifuging, dissolve it in hot water, saponify cold with 100 ml. 0.1*N* NaOH for 2 hr., acidify with 50 ml.

acetic acid, and precipitate after 5 min. with 25 ml. of 2*N* $CaCl_2$. Filter the Ca pectate through a tared paper, boil the filtrate 5 min., filter through the same paper, and wash free from chloride. Dry at 100°–105°C. Ca pectate X 176/195 = polygalacturonic acid. The filtrates are combined and evaporated to dryness. The residue is hydrolyzed for 14 hr. with HCl under reflux. Hexoses are determined in the hydrolyzate with Fehling's solution, and pentoses by conversion of xylose to furfural which is determined iodimetrically with $KBrO_3$ and KBr. This determination of pectin was verified by comparison with the potentiometric method of Deuel and by determining COOH groups as CO_2 (McCready, Swenson, and McLaye). Results of analysis of some tanning materials were as follows:

Material	Percent on dry basis of				
	Tannin	Nontannin	Polygalacturonic acid	Hexoses	Pentoses
Wattle extract	73.7	14.9	2.9	.....	.....
Jugoslav chestnut extract	78.1	10.1	1.1	.....	.....
Spruce bark extracted					
with 0.6% Na_2SO_3	.....	.....	3.1	12.9	3.6
with 0.9% Na_2SO_3	.....	.....	4.7	11.5	3.4
and 0.9% $NaHSO_3$					
with water at 95°C.	.....	.....	3.1	.....	.....
with water at 70°	.....	.....	1.4	.....	.....
with water at 50°	.....	.....	none	.....	.....
Sumac (*R. typhina*)					
extracted with water					
at 95°C.	.....	.....	3.1	.....	.....
at 60°	.....	.....	2.1	.....	.....
at 40°	.....	.....	none	.....	.....

The content of polygalacturonic acid is much higher when extraction is done with NaOH. Removal of cations by ion exchange yields very viscous solutions, perhaps containing polysaccharides and decomposed pectins. The state of the pectins in the sulfite extract depends upon their degree of demethylation as well as the amount. Precipitation of pectin, a protective colloid, renders tannin difficultly soluble, so that it too precipitates to a large extent. L.M.

The Sulfite Extraction of Spruce Bark. A. Blazej and E. Markusovska. *Ibid.*, **3**, 43–52 (1958); see preceding abstr.—The undesirability of sulfite extraction is discussed. The results of the usual hide powder analysis of the extracts are in contradiction to the practical experience of tanners. Binko and Kolar (preceding abstract) tried to determine substances that are fixed by hide powder but do not tan, e.g. polyuronides. In the present study spruce bark as received and after extraction with water or with 8 different quantities of a 1:1 mixture of $NaHSO_3$ and Na_2SO_3 was analyzed by successive extractions with different solvents. The bark was extracted first in a Soxhlet, 3 hr. with benzene, yielding resins; next with ethanol, 4 hr. (sugars, tannins, and "other compounds"); next with water, 2 hr. at 100°C. (polyuronides—this extract

contained no tannin); next 0.05*N* HCl under reflux for 30 min. (more polyuronides, pentosans, and hexosans); then 2% HCl (more pentosans and hexosans). Finally the lignin was determined after hydrolyzing the insoluble residue from the HCl extraction with 72% H_2SO_4 for 2.5 hr. at 24°–26°C. The extraction of the bark before subjecting it to this system of analysis was done by treating 60 g. bark in a Koch-Korner apparatus for 5.5 hr. with 2000 ml. water, or with 550 ml. water followed by 700 ml. of the sulfite-bisulfite solution and finally 700 ml. water. Percentages of "tannin" found in the bark, from analysis of the extracts, were as follows:

% Na_2SO_3	none	1.0	1.5	2.0	3.0	4.0	5.0	?	11.5
% $NaHSO_3$	none	1.0	1.5	2.0	3.0	1.0	5.0	?	11.5
% tannin	8.8	10.6	11.0	10.9	10.7	11.1	13.2	14.1	17.9
% nontannin	3.6	3.5	3.2	3.5	3.6	3.6	3.7	3.2	3.8

Only the tannin extracted by water can be considered real tannin. The additional "tannin" gained by sulfiting is mostly polyuronides, hemicelluloses, and a little disaccharide. An additional alcohol extraction of the extracted bark gave 0.22 to 0.5% disaccharides, 0.28 to 0.56% polyuronides, 0.6 to 3.1% hexosans, and in the last 3 samples 0.9 to 2.2% lignin. **Analysis of Tanning Barks and Woods.** A. Blazej. *Ibid.*, 119–26.—Only 10% of the spruce bark produced is utilized for tanning; the rest is wasted or burned. The same holds for the (waste?) wood. A rational analysis of barks and woods is needed. Bark from an 80-year-old spruce tree stored in the laboratory for 1 yr. was analyzed by the author's procedure. It contained water, 14.5%; resins, 3.1%; alcohol extract, 11.2% including 7.7 tannin by the filter bell method, 1.1 monosaccharide, 1.4 oligosaccharide, and 1.0 "other compounds"; polygalacturonic acid (Carre-Heynes method), 0.7% in water extract and 3.1% in 0.05*N* HCl extract; cellulose (Kürschner-Hoffer method), 21.2%; lignin (König-Komarov method), 25.3%; pentosans (Tollens method), 8.2%; hexosans, 9.5%; nitrogen, 0.9%; and ash, 2.3%. L.M.

The Fixation of Vegetable Tannins by Hide Powder Chromed to Various Degrees with Basic Chlorides and Perchlorates of Chromium. K. H. Gustavson. *J. Soc. Leather Trades' Chemists*, **42**, 191–205 (1958).—The rate and extent of fixation of vegetable tannins by hide powder are markedly increased by cationic Cr tanning the hide powder to various Cr contents with solutions corresponding to the empirical formula: $Cr_2(OH)_{6-n}X_n$, where X = Cl or ClO_4 and $n \geq 4$. Additional binding of vegetable tannins increases rapidly with increasing Cr content of the prechromed hide powder up to 3–4% fixed Cr_2O_3. Pretanning to Cr levels beyond this induces no additional vegetable tannin fixation. In addition to formation of Cr–vegetable tannin complexes by displacement of coordinated groups in the Cr complex and by coordination directly with Cr atoms of the complex, activation of basic protein groups as sites for additional tannin fixation is an important factor. Pretanning with solutions of extremely basic Cr chlorides or perchlorates causes smaller vegetable tannin pickup than pretanning with cationic Cr complexes. The competition between uncharged Cr complexes and vegetable tannins for keto-imide

groups of collagen will occasionally result in a diminished binding capacity for vegetable tannins. J.M.C.

Importance of Water Solubles for the Evaluation of the Quality and Kind of Tannage of Vegetable-tanned Sole Leather. A. Blazej. *Kozarstvi*, **7**, 36–39 (1957).—Sole leather produced by "slow" tannage (defined as a 6- to 12-month tannage in cold liquors of 28° to 35°Barko.) can be distinguished from leathers of "combination tannage" by their lower water-solubles content. Best sole leather contains from 10 to 15% water solubles. The Czechslovak specification for maximum water-soluble matter in slow-tanned leather is: bend, 10; shoulder, 12; and belly, 14%. Yearly averages for water-soluble matter found by analysis (1946–55) were: bend, 6.7–8.8; shoulder, 8.3–10.8; and belly, 9.4–11.3. The maximum values set by the Czechoslovak standards are fully justified, and the higher maxima proposed by Kubelka (15%) and Stather (12%) are not. Maximum permitted water-soluble matter in combination-tanned sole leather is: bend, 15; shoulder, 17; and belly, 19%. The yearly average values found by analysis were: bend, 11.9–14.3; shoulder, 13.4–15.8; and belly, 14.1–17.4%. The first Czechoslovak syntans, K_1 and K_2, affected water solubles unfavorably. The later syntans K_1D and K_2D (Binko and Hejcl, *JALCA*, **51**, 505 [1956]) are better, but the use of more than 30% of these syntans, figured on the total tannin, impairs the quality of sole leather and raises the water solubles. The high degree of sulfitation of spruce bark during extraction of tannin also has had an unfavorable effect on water-solubles content. When the authorized quantity of total tannin was increased from 32 to 36% of the pelt weight, with syntans limited to 25 to 30% of the total tannin, the annual average for water solubles declined from 13.6 to 12.8%. It is pointed out that comparison of these standards and analytical data with those of other countries is very difficult because of differences in methods of determining water solubles. L.M.

The Amino Acid Composition of Fractionated Cortical Cells from Wool. D. H. Simmonds and J. J. Bartulovich. *Textile Research J.*, **28**, 378–81 (1958).—Two cortical-cell fractions separated from wool after treatment at 30°C. for 50 hr. with 6*N* HCl have been analyzed for their amino acid composition. The heavy fraction was significantly richer than the light fraction in amide nitrogen, cystine, serine, and proline, but was deficient in alanine, glutamic acid, glycine, leucine, lysine, phenylalanine, and tyrosine. Both the cortical-cell fractions were richer than the original wool in cystine, lysine, and proline. The acid-soluble material was richer in glycine, phenylalanine, serine, and tyrosine. R.M.L.

The Variability of Set in Keratin Fibers. T. Mitchell and M. Feughelman. *Textile Research J.*, **28**, 453–6 (1958).—The amount of "permanent" set in a number of wool fibers was measured, the fibers being strained 40% for 1 hr. in distilled water at 100°C. and then released slack for 1 hr. in water. A direct correlation appears to exist between the amount a fiber supercontracts in a concentrated LiBr solution and the amount of set as measured by the one-hr. index. The setting process is time-dependent, with the time constant being quite variable from fiber to fiber. Coarser fibers have a strong tendency toward a longer time constant, while finer fibers tend to have a shorter time constant. R.M.L.

PATENTS

Method of Separating Lignosulfonic Acids. U. S. Pat. 2,838,483. Leif Jantzen, Oslo, Norway, assignor to Arthur C. Trask Company, a corporation of Illinois. Appl. Apr. 1, 1955.—2. The method of treating sulfite liquor from a sulfite paper pulp process to separate selectively alpha-high molecular weight lignosulfonic acids and beta-low molecular weight lignosulfonic acids therefrom which comprises contacting said liquor with chrome tanned hide in an amount of about 2 parts by weight of the tanned hide per part of alpha acids for a time sufficient to combine chemically said alpha acids with the tanned hide, washing said tanned hide with an alkali to remove the alpha acids therefrom as salts and activate the tanned hide for subsequent reaction with the beta acids, again contacting said liquor from which the alpha acids have thusly been substantially removed with the tanned hide for a time sufficient to combine chemically said beta acids with the tanned hide, and washing said tanned hide with an alkali to remove the beta acids therefrom as salts.

Process and Product of Tanning with Condensation Products of Polyhydric Phenols with Methylol Dicyandiamide or Methylol Dicyandiamidine Compounds. U. S. Pat. 2,836,480. Ernst Honold and Arthur Miekeley, Frankfurt am Main, Fechenheim, Germany, assignors to Cassella Farbwerke Mainkur Aktiengesellschaft, Frankfurt am Main, Fechenheim, Germany, a company of Germany. Appl. Jan. 12, 1954.—1. In the process of tanning a skin, the steps which comprise adding, at a temperature range between 20 and 50° C., 0.5—1 mole of a polyhydroxy benzene selected from the group consisting of dihydroxy benzene and trihydroxy benzene to an aqueous solution of 1 mole of a compound selected from the group consisting of monomethylol dicyandiamide and monomethylol dicyandiamidine, condensing at said temperature range the compound and the polyhydroxy benzene in an acid medium and tanning a skin with the resultant solution.

Method of Preparing Filaments and Sheets from Procollagen. U. S. Pat. 2,838,363. Arthur Veis and Jerome Cohen, Chicago, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois. Appl. Oct. 19, 1954.—1. The method of producing a material of relatively high wet strength from procollagen, comprising converting an aqueous acid solution of procollagen to a gel by dialyzing said solution against water, said dialysis being carried out at a rate slow enough to form a gel having a substantially homogeneous appearance to the naked eye, aging the homogeneous gel in water to increase its cohesive strength, and then applying stress with a directional orientation to the aged gel while exuding water therefrom.

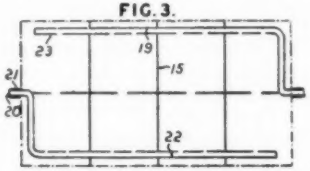
Process of Retanning Mineral-tanned Leather with Resorcinol-Formaldehyde. U. S. Pat. 2,840,445. Douglas K. Severn, Norwich, Conn., assignor to Koppers Company, Inc., a corporation of Delaware. Appl. June 9, 1954.—1. A process for simultaneously retanning and increasing the shrink temperature of mineral pre-tanned leather comprising the steps of wetting said

leather with water in excess of the amount said leather will absorb, draining said leather, intimately admixing said leather with resorcinol in an amount of approximately 2 to 5 percent based on the wrung out leveled weight of said pretanned leather, thereafter contacting the admixture of wet leather and resorcinol with formaldehyde in an amount of from approximately 1.5 to 3.0 moles per mole of said resorcinol, and establishing and maintaining the pH of said system in the range of approximately 6.0–7.5 until the supply of resorcinol and formaldehyde in the liquid present in said system is exhausted, the resulting retanned leather being capable of withstanding shrinkage in boiling water.

Mildewproofing of Leather. U. S. Pat. 2,838,426. Sverre Dahl, West Hyattsville, Md., and Arthur Milton Kaplan, Waban, Mass., assignors to the United States of America as represented by the Secretary of Commerce. Appl. Feb. 18, 1957.—3. The process of rendering leather mildewproof comprising the steps of making a solution comprising approximately 5 percent of bis(4-nitrophenyl) carbonate, 50 percent dioxane, 10 percent neat's-foot oil and 35 percent chloroform, diluting the solutions to provide a concentration of said bis(4-nitrophenyl) carbonate of from 0.3 to 0.6 percent by weight of dry leather, impregnating the leather by immersing in the diluted solution until the desired concentration of said carbonate is obtained and drying said impregnated leather.

Leather-dressing Tables. Brit. Pat. 793,424. Leportier, P. Appl. Sept. 27, 1956.

FIG. 3.



—A table for drying and dressing leathers, skins, or the like, pivotally mounted about a horizontal axis so that it can be used in a horizontal or vertical position, and is filled by a hot circulating fluid, such as hot water admitted and removed through rotary joints coaxial with the said axis. The circulation inside the table is shown in Fig. 3, where hot fluid enters through a conduit 19 coupled to a rotary joint 20 incorporated in a pivot 21, escapes through orifices 23 and is guided by the transverse partitions 15 to a return conduit 22. The table can be vertically swivelled about the central axis on the pivots 21.

Artificial Leather. Brit. Pat. 793,888. Novacel. Appl. Jan. 31, 1956.—Artificial chamois leather is moulded from a mixture of viscose, soluble crystals, e.g. sodium sulphate, and fibres, e.g. hemp or flax, in a mould having a honeycomb pattern in relief to impart a goffered appearance to the leather. The material may be moulded on to one or both sides of a layer of cloth. The mould may impart a pattern, e.g. a trade mark. The material is coagulated by heating, e.g. in an oven, by direct electric heating or by high-frequency heating. The coagulated material is removed from the mould, washed to remove the soluble crystals, bleached, treated with a dressing, plasticised, and dried.

Making Leather. Brit. Pat. 793,603. Farbenfabriken Bayer Akt.-Ges. Appl. Mar. 7, 1956.—A skin is treated before, during or after tanning with a mixture comprising an aqueous polymerization emulsion of a compound containing at least one polymerizable double bond, at least 2 per cent (based on the weight of the polymer) of an emulsifier and a vegetable and/or synthetic tanning agent: the emulsifier is cationic or non-ionic and may be partially replaced by an anionic emulsifier containing a sulphonic acid group in the molecule, as used in the parent Specification. The process may be used in acid or neutral conditions. Suitable polymerization emulsions and tanning agents are those used in the parent Specification: specified cationic or non-ionic emulsifiers are aliphatic or aromatic polyoxyethyl ethers, carboxylic acid polyoxyethyl esters or N-polyoxyethel substituted amines, containing a large number of ethylene oxide units per molecule and water-soluble salts or quaternary products of long-chain aliphatic amines. The process may, e.g., be applied to chrome-, semi-chrome- and vegetable-synthetically-tanned leather, and in examples: (1) chrome tanned cowhide is treated with a mixture of a copolymerization emulsion of dichloroethane and butyl acrylate with a cetyl alcohol/ethylene oxide condensate emulsifier and a naphthol sulphonic acid/phenol/formaldehyde tannin; (2) bastard leather pretanned with myrobalan is treated with a mixture of a similar copolymerization emulsion with a stearylamine/ethylene oxide condensate emulsifier transformed into quaternary form with benzyl chloride and a sulphonated quebracho tanning agent, and retanned with an aryl sulphonic acid/formaldehyde condensate; (3) chrome tanned calf skin is neutralized, fat-liquored with sulphited and unsulphited oils, retanned with the retanning agent in (2) and treated with a mixture of a copolymerization emulsion of butadiene, acrylonitrile and styrene with a cetyl alcohol/ethylene oxide condensate emulsifier in admixture with the sodium salt of an alkyl sulphonate containing 8–16 carbon atoms, and a tanning agent: finally the leather was retanned with the retanning agent of (2), and fat liquored as before. The parent specification is Pat. 756175.

Tanning and Retanning. Brit. Pat. 792,549. Farbenfabriken Bayer Akt.-Ges. Appl. Nov. 8, 1955.—In manufacturing leather an amphoteric condensation product of a polyhydric phenol, an amine or ammonia and an aldehyde containing one or more mols. of amine or ammonia per mol. of phenol is used as a tanning agent and the leathers in the tanning liquor are neutralized to the isoelectric point. The amine or ammonia may be used in salt form. The tanning agents may be used in the same tanning liquor as inorganic tanning agents such as chrome, zirconium, iron or aluminium tanning agent and may be compatible with the sulphates as well as the chlorides of these metals. They may also be used to retan leathers tanned with vegetable (quebracho or chestnut and mimosa), synthetic (e.g urea formaldehyde, dicyandiamide-formaldehyde, melamine-formaldehyde, and phenol-formaldehyde resins or the product otbained by sulphonating a low molecular weight phenolic resin) and inorganic (sulphite waste liquors, iron, chromium, aluminium, or zirconium) tanning agents. Half the anionic tanning agent may be saved if desired by replacing it with the amphoteric agent used for retanning. It may be desirable to begin tanning with an inorganic tanning agent such as chrome and add the tanning agent of the invention to the liquor to complete tanning. The tanning agents of the invention and their sulphates and salts of organic acids are soluble and tanning can be carried out in the presence of considerable quantities of common salt and

acids, e.g. hydrochloric, and the products may be easily dyed with acid and anionic dyestuffs. Prior to neutralization proper it is desirable to add mild alkalies such as alkaline salts of weak acids, e.g. ammonium acetate. Neutralization to *p*H 7–7.5 may be carried out with further quantities of mild alkalies or with ammonia or soda. At this *p*H the leathers should not be unnecessarily exposed to the air. Examples are given in which there may be used tanning and retanning agents prepared by condensation of (a) resorcinol, catechol or pyrogallol with ethanolamine, allylamine, dimethylamine or morpholine and formaldehyde; or (b) resorcinol, catechol or pyrogallol, ammonium chloride and formaldehyde. The hides may be drummed prior to tanning with a mixture of salt and hydrochloric acid. Specification 747,094 is referred to.

ERRATA

The second line under the table on page 517 of the September 1958 number should have read: "The hydroxyproline/total nitrogen ratios . . .", not "The hydroxyproline solidus total nitrogen ratios . . .".

The title of the second abstract on page 533 of the September 1958 number should have read: "Studies on the Change of the Composition *and* the Tanning Properties of Skin Tissue."

The heading of the last abstract on page 610 of the October 1958 number should have read: **"The Configuration of Polypeptide Chains in Proteins.** R. B. Corey and L. Pauling. *Proc. Intern. Wool Textile Research Conf., Australia, 1955 (publ. 1956)*, **B**, 249–67."

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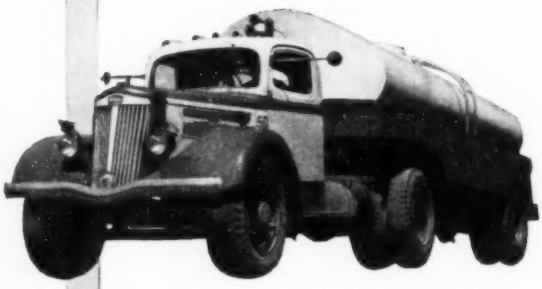

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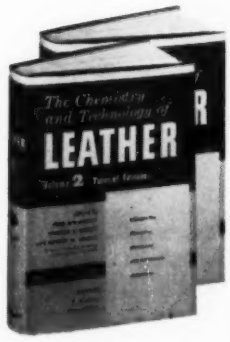

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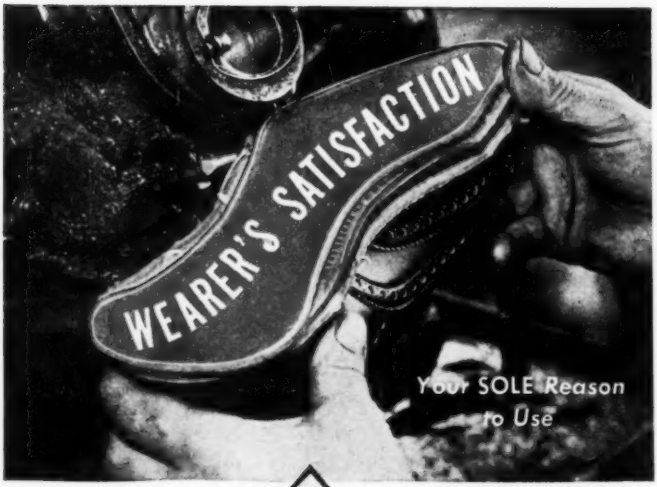

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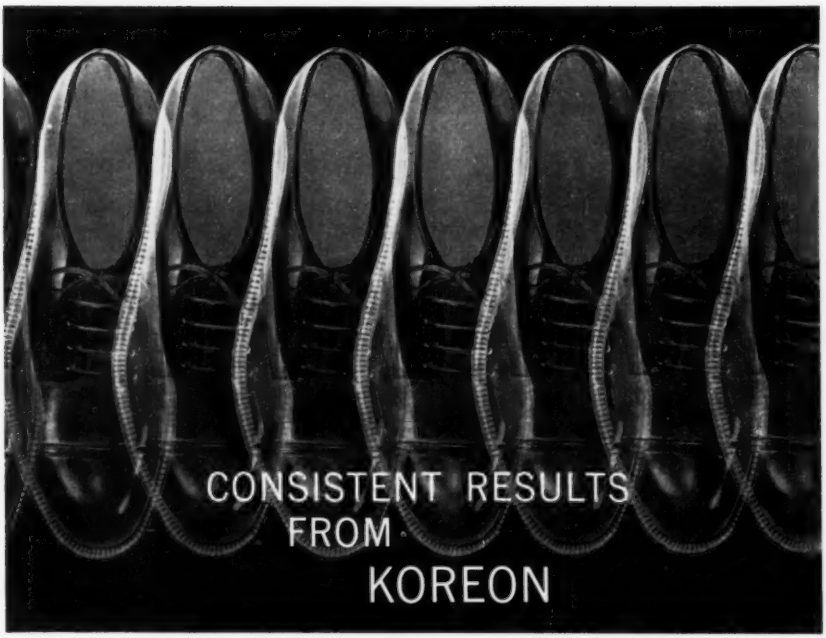

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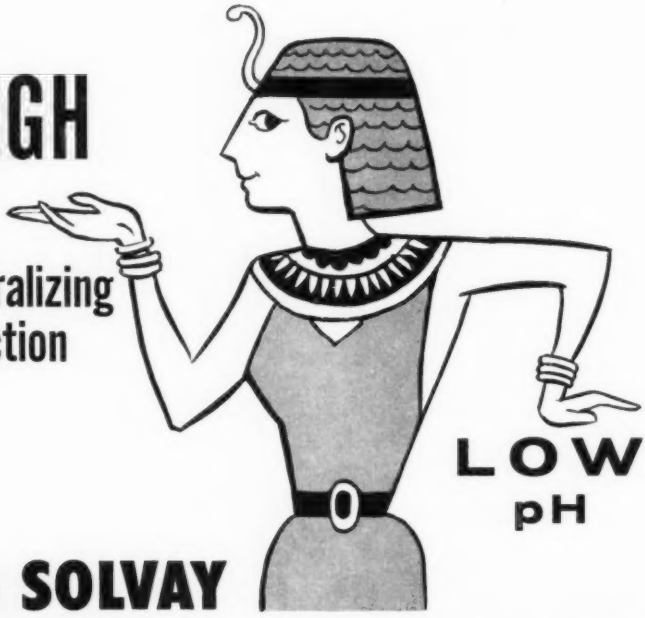

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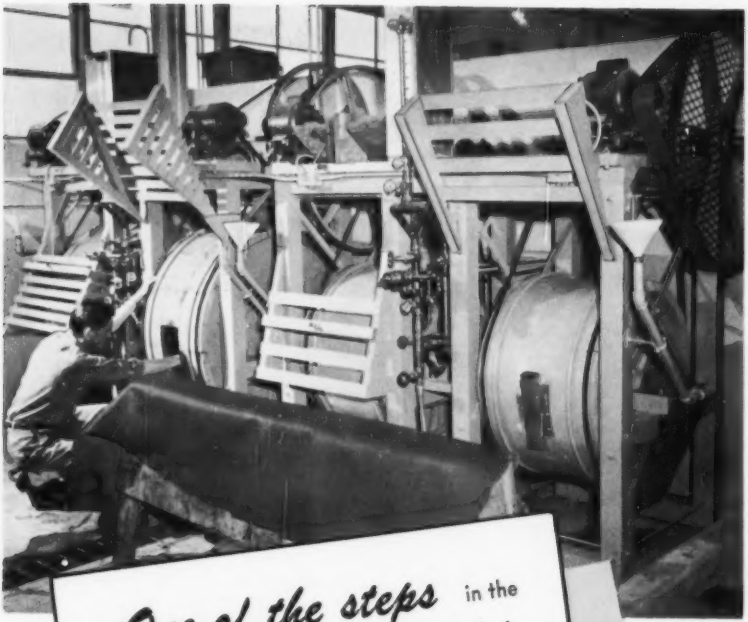

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